

Evaluation of Solid Adsorbents for Collecting
Atmospheric Chlorinated Hydrocarbons

South Carolina Univ. Columbia
Dept. of Chemistry

Prepared for

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Research Triangle Park, NC

Jul 80



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KEYWORDS: *Pesticides, *Chlorine organic compounds,
*Adsorbents, *Air pollution sampling.

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EVALUATION OF SOLID ADSORBENTS
FOR COLLECTING ATMOSPHERIC
CHLORINATED HYDROCARBONS

BY

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ABSTRACT

The comparative efficiency of polyurethane foam (PUF) and Tenax-GC resin for collecting polychlorinated biphenyls (PCB) and chlorinated pesticides from 300-1600 m³ air was determined by side-by-side sampling with each adsorbent in the city of Columbia, South Carolina. Air was pulled through a glass fiber filter followed by front and backup adsorbent traps containing PUF (two 7.9-g plugs) or Tenax resin (two 10-g portions). Each trap was analyzed separately to determine the penetration of chlorinated hydrocarbon vapors. Low molecular weight PCB (Aroclor 1016) was effectively retained by both adsorbent systems in a 24-36 hour sampling period (500-750 m³ air). The ratio of Aroclor 1016 on the front:backup traps was 10:1. Hexachlorobenzene (HCB) was very poorly retained by PUF but efficiently collected by Tenax. Negligible proportions (<5%) of the higher molecular weight PCB (Aroclor 1254) and pesticides (chlordane, toxaphene) penetrated through to the second adsorbent traps. Tenax was slightly more efficient than PUF for retaining Aroclor 1016 and continued to retain HCB effectively up to at least 1300 m³.

Average concentrations of chlorinated hydrocarbons (10⁻⁹ g/m³) measured from May 1977 - August 1979 in Columbia were: Aroclor 1016 = 3.3, Aroclor 1254 = 1.6, HCB = 0.31, chlordane (cis- + trans-isomers) = 1.4, and toxaphene = 15. Toxaphene levels showed the greatest variability, being an order of magnitude higher during the late summer than during the rest of the year. The average difference between Aroclor 1016 levels determined by Tenax and PUF collection was 14%, the higher values being with Tenax. HCB concentrations determined by Tenax collection were several times higher than those measured with PUF, a reflection of the more efficient retention of HCB by Tenax. Average differences between Aroclor 1254, chlordane, and toxaphene levels determined by the two methods were < 5%, with no trend toward high or low results with either adsorbent. Average relative standard deviations for duplicate or triplicate collections with one adsorbent system ranged from 8-22%, depending on the compound. The precision appeared to be limited by the analytical methodology rather than the sampling technique.

Penetration of individual PCB isomer vapors through 1-cm thick sections of PUF was investigated in a laboratory experiment. PCB isomers applied as a spike to the front of the foam column were eluted in distinct bands by the high volume airflow in a similar manner to the movement of vapors through a gas chromatographic column. The penetration of PCB vapors was greater for the lower molecular weight isomers and was linear with total air volume. Fifteen cm of PUF (cross sectional area = 45 cm²) was sufficient to retain 90% of a dichlorobiphenyl isomer spike in a 24-hour sampling period (600 m³ air).

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ACKNOWLEDGEMENT

We thank the South Carolina Department of Health and Environmental Control for their assistance with sampling pump calibrations.

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SECTION 1

INTRODUCTION

Determination of low part-per-trillion (10^{-9}g/m^3) levels of polychlorinated biphenyls (PCB) and pesticides in ambient air requires that hundreds of cubic meters of air be sampled to provide enough material for analysis. For this reason, as well as for greater convenience in field handling, solid adsorbent collectors have supplanted low flow rate bubblers and impingers, which are capable of sampling less than $50\text{ m}^3/\text{day}$. A thorough review of sampling methodology for airborne pesticides and PCB has been published by Lewis (1976). Polyurethane foam (PUF) has become a widely-used adsorbent for sampling airborne PCB since its initial use for this purpose in 1974 (Bidleman and Olney, 1974a,b). PUF has several advantages: it is cheap, easily cleaned up, and as a one-piece plug it is easy to handle in the field. PUF is also highly retentive for many chlorinated pesticides and high molecular weight PCB (Bidleman and Olney, 1974a; Rice et al., 1977; Turner and Glotfelty, 1977; Lewis et al., 1977). The collection efficiency of any solid adsorbent bed depends on the volatility of the organic compound being sampled and on the total volume of air pulled through the bed, and for PUF, incomplete retention of the lighter PCB isomers and polychlorinated naphthalenes (Hallowaxes) has been reported (Lewis et al., 1977). This study was undertaken to determine the collection efficiency of solid adsorbents for PCB and chlorinated pesticides of differing volatilities. Two approaches were taken:

1. The comparative collection efficiency of three solid adsorbents was evaluated by sampling urban air for 24 - 48 hours ($300 - 1500\text{ m}^3$ air). Air was pulled through a glass fiber filter followed by front and backup adsorbent traps containing PUF, Tenax-GC resin, or XAD-2 resin. Collection efficiencies were determined by separately analyzing the front and backup traps. Sampling reproducibility was evaluated by duplicate or triplicate collections with the same adsorbent system.

2. The movement of individual PCB isomers through a PUF column was investigated under controlled conditions in the laboratory. PCB vapors were drawn through a column packed with 1-cm thick sections of PUF, and the penetration of the PCB isomers was determined as a function of flow rate and total air volume by analyzing the individual PUF slices. This approach showed that a solid adsorbent collector functions much like a gas chromatographic system, in which vapors move through the column in a predictable manner governed mainly by volatility and total air volume.

Accuracy in determining airborne PCB and pesticides requires not only an efficient collection system but also selective analytical methods.

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Reliable identification of organochlorines is made more difficult by the multicomponent nature of some of these materials. The chlorinated insecticides toxaphene and chlordane are complex mixtures which are major constituents of the airborne organochlorines in the southeastern United States (Bidleman *et al.*, 1978). These pesticides are inseparable from PCB by gas chromatography alone, and their presence can seriously bias the estimation of the PCB content of urban air. The application of a four-fraction silicic acid column method for separating PCB from chlorinated pesticides is discussed in Section 2C. Also presented in this section are analyses of ambient air samples using a 30 m glass capillary column, which show that PCB identification by conventional packed column GC remains uncertain even after extensive sample fractionation and pretreatment.

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SECTION 2

MATERIALS AND METHODS

A. SOLID ADSORBENTS

Three adsorbents were selected for sampling airborne PCB and chlorinated pesticides. Two of the adsorbents were PUF and Tenax-GC resin, a porous polymer of 2,6-diphenyl-p-phenylene oxide. Tenax was a logical choice despite its exorbitant cost (\$90/15 g) because it has been used extensively in recent years to trap volatile organics under low volume sampling conditions (Zlatkis *et al.*, 1973; Bertsch *et al.*, 1974; Pellizzari *et al.*, 1975, 1976; Sydor and Pietrzyk, 1978). The elution of low molecular weight chloroalkanes through a Tenax bed is controlled by vapor pressure, with log retention volume being linearly related to the reciprocal of the absolute temperature (Vidal-Madjar *et al.*, 1978). Initially we had planned to test a liquid-coated support as the third collector, since these materials had been used to trap airborne pesticides and PCB in earlier studies (Compton, 1972, 1973; Beyermann and Eckrich, 1974; Harvey and Steinhauer, 1974). However, Rohm and Haas XAD-2 resin (a styrene - divinylbenzene copolymer) was chosen as an alternative, and near the end of this study some preliminary collection efficiency data were obtained with this adsorbent. Several XAD resins are effective for collecting low molecular weight organic vapors under low volume conditions and in fact have a higher surface area than Tenax: 100-850 m²/g for XAD-1 through XAD-4 *vs.* 19 m²/g for Tenax (Sydor and Pietrzyk, 1978). XAD-2 resin has been reported to effectively collect 83% of the very light PCB mixture Aroclor 1221 even for air volumes as high as 1400 m³ (Doskey, 1978).

Polyurethane foam preparation

Polyurethane foam (PUF) was obtained from Olympic Products Corporation, Greensboro, North Carolina. Type 3014 PUF, which has a reported density of 1.4 lbs/ft³ (0.022 g/cm³), was selected for evaluation. This foam is sold in many furniture stores under the trade name Conefoam[®], and has a density equivalent to that of foams that we have used in previous studies (e.g. Bidleman *et al.*, 1974a). The measured density (0.023 g/cm³) of the type 3014 PUF agreed with the manufacturer's specifications.

The following method was used to cut foam plugs from 7.6-cm thick sheet stock: The foam sheet was compressed between two plywood boards, the upper board containing a number of 8.3-cm holes. Plugs 7.6 cm diameter x 7.6 cm thick (weight = 7.9 g) were then cut with a circular hole saw mounted on a drill press. Before using, the saw was soaked in acetone to remove paint and grease and then baked in a muffle furnace overnight at

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500°C to ensure complete removal of potentially contaminating organics. Less tearing of the foam occurred if the teeth of the saw were first straightened to remove the "set" and if the saw was rotated in reverse of its normal direction. We found this method of cutting plugs superior to handcutting with scissors or stamping them out with a press and sharpened metal cylinder.

Foam plugs were soxhlet extracted with reagent grade acetone (24 hrs) followed by pesticide quality petroleum ether (24 hrs) and dried in vacuo, as described by Bidleman and Olney (1974a). The plugs were stored in 10.2-cm diameter x 7.6-cm deep seamless cans, with friction-fit lids ("ointment tins", Eastern Scientific Company, Providence, Rhode Island). Six plugs were prepared at a time, and 1-2 plugs out of each set were extracted and analyzed to assess the background levels of electron-capture sensitive compounds contributed by the foam, the solvents, and the laboratory handling procedures. Petroleum ether extracts of clean foam showed 2 early-eluting GC peaks (Bidleman and Olney, 1974a) (Fig. 1) which were removed either by passing the extract through a 4-g column of activity grade III alumina, or by shaking the extract with concentrated or 7% fuming H₂SO₄. PCB and most chlorinated pesticides are stable to the latter treatment (Section 2C). Peaks remaining after acid treatment were calculated as Aroclors 1016 and 1254 (Fig. 1). Mean blanks for 14 plugs prepared over a period of several months were: 9.1 ± 6.9 ng Aroclor 1016 and 4.6 ± 2.6 ng Aroclor 1254 (Table 1). These levels are very low. We attribute our success to extreme care in handling the plugs after cleanup, in particular to the use of the vacuum desiccator for drying the extracted plugs (Bidleman and Olney, 1974a).

Tenax-GC and XAD-2 resin preparation

Tenax-GC (manufactured by AKZO Research Laboratories, Holland) is a porous polymer GC-column packing that is based on 2,6-diphenyl-p-phenylene oxide. Two mesh sizes, 60/80 and 35/60, were purchased from Applied Science Laboratories (State College, PA). For cleanup, the Tenax was placed in pre-cleaned 43 x 123 mm cellulose extraction thimbles and soxhlet extracted for 24 hours with pesticide-quality petroleum ether. The first extract was analyzed by electron-capture gas chromatography (EC-GC) after alumina and sulfuric acid cleanup (Section 2C). Different lots of Tenax contained 70-225 ng/g Aroclor 1016 and 25-45 ng/g Aroclor 1254. The extracted thimbles of Tenax were vacuum-dried as for PUF plugs and were stored in sealed glass jars. Second extractions of the dried Tenax gave average blanks only slightly higher than those of PUF plugs (16 ± 17 ng Aroclor 1016 and 11 ± 8.8 ng Aroclor 1254 for 10-g portions of Tenax, n = 10) (Table 1).

XAD-2 resin (20/50 - mesh), a polymer consisting of styrene-divinylbenzene with a pore size of 90Å and a surface area of 300 m²/g (Sydor and Pietrzyk, 1978) was obtained from Rohm and Haas Corporation (Philadelphia, PA) under the Mallinckrodt label. Doskey (1978) found that the blank values for XAD-2 were improved by first drying the resin to crack the surface and partially expose the interior. Accordingly, we vacuum-dried the resin at 40-50°C for 24 hours, then soxhlet extracted the resin in the

same manner as for Tenax. Second extractions of 20-g portions of XAD-2 yielded average blank values ($n = 2$) of 19 ng Aroclor 1016 and 13 ng Aroclor 1254. These blanks are about the same as those obtained for Tenax and slightly higher than PUF background values (Table 1).

PCB blanks for all three adsorbents were negligible in comparison to the quantity of PCB sampled in a 24-hour period in the city of Columbia. Typical ambient concentrations of 2 ng/m³ Aroclor 1254 and 3 ng/m³ Aroclor 1016 yielded 1000-1500 ng PCB for a 500 m³ air volume, about 50-100 times the average background values.

An important consideration with any solid adsorbent is whether a clean adsorbent will remain clean upon storage. We have never encountered difficulty with polyurethane foam; plugs which were stored in sealed cans for a year yielded blank values no different from those of new, precleaned plugs. However, in a recent report of Tenax as an adsorbent for collecting volatile organics the authors presented data showing that analytical artifacts were obtained from clean Tenax that had been stored in sealed glass tubes (Juarez and Bertsch, 1978). Presumably these artifacts were caused by organic contaminants deep within the Tenax resin bead diffusing to the previously cleaned bead surface during the storage time. To check for possible PCB contamination by this effect, we extracted portions of precleaned Tenax, dried and stored the resin for one month in a sealed jar and then reanalyzed the resin. No increase in background PCB levels was observed after the storage period (Table 2).

Glass fiber filter preparation

Gelman type A/E glass fiber filters were used to precede the solid adsorbent traps. These filters are capable of collecting airborne particles down to 0.015 μ m radius with 98% efficiency (Butcher and Charleson, 1972). The 10-cm diameter or 20 x 25-cm filters were wrapped loosely in aluminum foil and baked overnight in a muffle furnace at 400°C to remove organic contaminants. Baking the filters at higher temperatures caused them to become brittle and crack during sampling.

B. SAMPLING SYSTEMS

Solid adsorbent columns and filter holders

Collection units to hold PUF plugs (Fig. 2) were made from Gelman 10-cm diameter cast aluminum filter holders (Gelman part #16050). Paint was removed from the filter holder by sandblasting or soaking in chromic acid. The rear of the filter holder was milled out to 7.3 cm diameter and a 20-cm length of 7.0 cm i.d. aluminum pipe was attached by heliarc welding. The other end of the pipe was reduced to 5-cm o.d. to fit into a length of 5-cm i.d. flexible hose (Flexaust[®], Niantic Rubber Company, Cranston, RI), which was used to connect the collection unit to the air pump. A piece of wire screen placed at the exit end of the sampler barrel prevented the PUF plugs from seating directly against the constricted end of the tube (Fig. 2). Air flow was thus maintained over the entire cross section of the foam column. Gelman filter holders come equipped with a black foam

rubber ring, which creates an airtight seal between the glass fiber filter and the stainless steel support screen. This ring was removed and replaced by a non-contaminating red silicone rubber gasket (Niantic Rubber Co., Cranston, RI). Effective rain shields were made from aluminum cooking pots and long bolts, obtained at local hardware stores (Fig. 3).

The collectors allowed us to sample with two 7.6-cm diameter x 7.6-cm thick PUF plugs preceded by a 10-cm diameter filter. Typical flow rates through this system were 0.35 - 0.5 m³/min. Higher flow rates, on the order of 0.6 m³/min could be achieved by replacing the 10-cm diameter filter with a larger 20 x 25-cm one. To do this, a 20 x 25-cm stainless steel filter holder (General Metals Works, Cleves, OH, model FH-2100) was adapted to fit snugly on top of the collection unit shown in Fig. 2. An airtight seal was made between the metal surfaces with a silicone rubber gasket. The collection assembly with the larger filter holder in place is shown in Fig. 4.

Tandem cartridges (Fig. 5) for pellicular solid adsorbents (Tenax, XAD-2) were constructed from 8.3-cm i.d. aluminum pipe (6 mm wall thickness) and aluminum sheet stock. Two pieces of the pipe were milled to provide a slip fitting between the upper and lower sampling cartridges; an airtight seal was achieved with a silicone rubber gasket and four clamps. Solid adsorbents were retained in the cartridges by an 80-mesh stainless steel sieve, which was mounted in a groove milled on the inside of the aluminum pipe and epoxy glued into place. The top of the tandem trap was designed to mate with a 20 x 25-cm filter folder (shown in Fig. 4) and the bottom

TABLE 1. AVERAGE BLANK VALUES FOR PRECLEANED SOLID ADSORBENTS

		10 ⁻⁹ g	
	Adsorbent weight, g	Aroclor 1016 ^a	Aroclor 1254 ^a
PUF	7.9	9.1 ± 6.9 (14)	4.6 ± 2.6 (14)
Tenax-GC	10.0	16 ± 17 (10)	11 ± 8.8 (10)
XAD-2	20.0	15 ± 2.5 (2)	13 ± 2.3 (2)

(a) Total organochlorine residues calculated as Aroclors 1016 or 1254; columns give mean, standard deviation, and number of samples in parentheses.

was reduced to fit into a piece of 5-cm i.d. flexible hose. Flow rates through two 10-g Tenax (35/60-mesh) or 20-g XAD-2 resin traps and a 20 x 25-cm filter were 0.35 - 0.5 m³/min.

TABLE 2. BLANK VALUES FOR PRECLEANED TENAX RESIN

g Tenax	10^{-9} g		10^{-9} g	
	Immediately after cleanup ^a		After one month storage ^a	
	Aroclor 1016	Aroclor 1254	Aroclor 1016	Aroclor 1254
1.0	3.6	< 3	3.9	< 3
10.0	29	10	14	9

(a) Total organochlorine residues calculated as Aroclors 1016 or 1254.

TABLE 3. CHARACTERISTICS OF ROTRON INDUCTION MOTOR PUMPS^a

Pump	Model	Weight, kg	Free air
			capacity, m ³ /min
Spiral	SL2P2	12.3	1.56
Spiral	SL5P2	19.5	2.82
	DR-313AE58	19.5	1.56

(a) from company literature

Air pumps

For several years Gelman Hurricane 16003 pumps have been used by our group for air sampling. These pumps are capable of pulling 0.35 - 0.5 m³/min of air through a 10-cm diameter glass fiber filter and 2 PUF plugs. They are light and easily carried for field work. Unfortunately, Hurricane pumps have brush-type motors and are unreliable for long-term use. During the first year of this project several samples were lost because of pump failure caused by worn-out brushes. As alternatives to Hurricane pumps, three types of brushless induction motor pumps manufactured by Rotron Corporation (Woodstock, NY) were tested for air sampling. Characteristics of these pumps (Spiral SL2P2, Spiral SL5P2, and DR-313) are summarized in Table 3. Spiral pumps rely on the airflow through them for cooling, and these pumps were unable to maintain suction for long sampling periods without overheating. The problem was especially serious with the Spiral SL5P2 when operated at the high flow resistance offered by a 10-cm diameter filter and two adsorbent traps. DR-313 pumps are designed to maintain suction even at low flow rates without overheating, and four of these pumps have performed very reliably over the past year. A distinct disadvantage is their weight (19.5 kg).

Collection procedures

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Collections were made on the roof of the Physical Sciences Center, about 30 m above street level near downtown Columbia, SC (population 380,000). Loaded samplers were connected to the pumps via 5 m of flexible hose. The pressure drop, on the order of 75 - 100 cm H₂O, was measured with a Magnehelic gauge (Dwyer Instrument Company, Michigan City, IN) attached just behind the collector. The pressure drop was related to the volume flow rate through a calibration curve, constructed by replacing the sampling unit with an orifice calibrator (Federal Register, 1976). The orifice calibrator (BGI Incorporated, Waltham, MA) came equipped with several resistance plates, containing 5-13 holes. The 5-hole plate produced a flow rate of 0.65 m³/min, higher than the flows through the sampling trains. We therefore constructed additional resistance plates with fewer or smaller holes. The true flow rate through the calibrator with the resistance plates in place was determined by using a Roots positive displacement meter, made available to us by the South Carolina Department of Health and Environmental Control.

Each pump was individually calibrated at several flow resistances, and plots of pressure drop behind the calibrator vs flow rate were slightly different for each pump. A typical curve is shown in Fig. 6. At flow rates less than about 0.35 m³/min the calibration curves deviated from linearity, which made measurements of low flow rates difficult. The precision of flow rate measurements in the working range of the PUF, Tenax, and XAD-2 resin samplers was about 5-10%.

C. ANALYTICAL METHODS

Extraction, cleanup, and packed column GC analysis

Solid adsorbents were soxhlet-extracted with petroleum ether and glass fiber filters were refluxed with dichloromethane. Extraction times were at least three hours, and it was common practice to extract the samples overnight. Organochlorines in dichloromethane extracts were transferred to hexane by refluxing in a Kuderna-Danish apparatus. All solvents were pesticide-quality (Mallinckrodt Nanograde brand).

The extract in petroleum ether or hexane was concentrated in a Kuderna-Danish apparatus to 1-2 ml and transferred to a 4-g column of activity grade III alumina (6% added water) contained in a 1-cm diameter Chromaflex column (Kontes Glass Co., Vineland, NJ) and topped with 1 cm anhydrous sodium sulfate. Organochlorines were eluted with 20 ml petroleum ether, and the eluate was concentrated to 1-2 ml. The organochlorines were then separated into four fractions on a 3-g column of precisely deactivated (3.3% water) silicic acid. Details of this procedure are given in Bidleman et al. (1978). The organochlorines in each fraction are given in Table 4. Since publication of this article, we have accumulated more information on the distribution of organochlorines among the fractions. Lindane and α -HCH divide between fractions 3 and 4, with the greater part in fraction 4. Several components of technical chlordane coelute with PCB in fraction 2. This causes problems with

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Aroclor 1016 identification and is discussed in detail later.

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Fractions from the silicic acid column were shaken on a vortex mixer with 7% fuming sulfuric acid. PCB and most chlorinated pesticides are stable to this treatment (Murphy, 1972; Veierov and Aharonson, 1978). Most oxygenated compounds are removed, including phthalate esters, which are ubiquitous air pollutants and which give a strong electron-capture response (Giam *et al.*; 1975, 1978). The cleaned up fractions were analyzed by EC-GC on two of the following columns: 1.5% SP-2250/1.95% SP-2401; 4% SE-30/6% SP-2401; 3% OV-225 (Supelco, Inc., Bellefonte, PA). All columns were glass, 0.4 cm i.d. x 180 cm long, and were operated at 180°-210°C and 40-60 ml/min nitrogen flow. Initially, all work was carried

TABLE 4. ORGANOCHLORINES ELUTED IN A FOUR-FRACTION SILICIC ACID PROCEDURE

Fraction	Eluate	Organochlorines ^a
1	13 ml petroleum ether	hexachlorobenzene (HCB)
2	37 ml petroleum ether	Aroclors 1016 and 1254, p,p'-DDE, 10% of toxaphene components
3	80 ml petroleum ether	p,p'-DDT, <u>cis-</u> and <u>trans-</u> chlordane, 30-40% of toxaphene components
4	15 ml dichloromethane	p,p'-DDD, dieldrin, 50-60% of toxaphene components

(a) from Bidleman *et al.* (1978)

out using a Tracor-222 chromatograph equipped with DC-type EC detectors. Because of the limited linear range of this instrument, analyses were carried out isothermally to avoid the baseline drift that occurs during temperature programming. More recently, a Varian 3700 instrument with linearized EC detectors was used for both packed and capillary column analysis, and better resolution of PCB on a packed 3% OV-225 column was achieved by temperature programming from 180°-210° during the run.

To evaluate the precision of the analytical methods, a "synthetic air sample" containing HCB, Aroclors 1016 and 1254, p,p'-DDE, p,p'-DDT, cis- and trans- chlordane, and toxaphene was prepared and analyzed by packed column GC after silicic acid fractionation. The results (Table 5) indicated that relative standard deviations of 10-15% could be expected.

Interference of technical chlordane components with Aroclor 1016 determination

Chlordane, a cyclodiene insecticide commonly used for termite control,

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TABLE 5. ANALYSIS OF A SYNTHETIC "AIR SAMPLE" AFTER SILICIC ACID COLUMN SEPARATION

Organochlorine	ng Taken	ng Found	% Relative ^a s.d.	% Recovery
HCB	376	280	12	74
Aroclor 1016	4560	4333	15	95
Aroclor 1254	4540	4187	9	92
p,p'-DDE	550	423	7	77
p,p'-DDT	807	702	12	87
cis-chlordane	441	379	11	86
trans-chlordane	428	381	11	89
toxaphene	3070	2660	15	87

(a) 5 replicates

is widely dispersed in continental and marine air (Bidleman and Olney, 1974b; Bidleman *et al.*, 1976). Technical chlordane (TC) is a complex mixture containing at least 45 compounds, with two major components, cis- and trans- chlordane, accounting for about 43% of the total (Sovocool *et al.*, 1977).

Packed column gas chromatograms of the "PCB fraction" of Columbia, SC air samples (silicic acid column fraction 2, Table 4) showed several large peaks with retention times close to or overlapping those of Aroclor 1016, but whose peak heights were far out of proportion to those of an Aroclor 1016 standard (Fig. 7). Subsequent examination showed that these large peaks matched early-eluting compounds in the TC pattern (Figs. 8 and 9), and cis- and trans-chlordane were readily identifiable in the "pesticide fraction" (fraction 3, Table 4) from the silicic acid column (Figure 10). Although cis- and trans-chlordane are well separated from PCB on a silicic acid column, other TC constituents are not. The major interference of TC with Aroclor 1016 is posed by components which coelute with PCB in the silicic acid procedure and produce two peaks which overlap the Aroclor 1016 GC pattern. According to Sovocool *et al.* (1977), these peaks are due to heptachlor and a monochloro adduct of pentachlorocyclopentadiene with cyclopentadiene. In order to estimate the magnitude of this interference, analytical standards of TC and Aroclor 1016 were mixed in varying ratios (Table 6) and fractionated by the silicic acid procedures of Bidleman *et al.* (1978) and Armour and Burke (1970). The PCB fractions from the silicic acid procedures were treated

with 7% fuming sulfuric acid to remove polar contaminants and analyzed by EC-GC on 1.5% SP-2250/1.95% SP-2401 and 3% OV-225 columns. Chromatograms of these fractionated mixtures were compared with those of an Aroclor 1016 standard, and the apparent Aroclor 1016 content of the mixtures was calculated from peaks having matching retention times. At a TC:Aroclor 1016 ratio of 3, the error in determining Aroclor 1016 was about 35-65%, depending on the GC column used (Table 6). Chromatograms of Aroclor 1016 contaminated with TC components are shown in Fig. 11. In environmental samples PCB chromatograms often appear different from those of standards, and these differences are commonly ascribed to selective "weathering" of PCB components or to greater volatilization of higher isomers. This study shows that altered patterns may also be caused by underlying organochlorines that are not PCB, in this case TC components.

Preliminary results indicate that treatment with alcoholic KOH may eliminate some of the interference posed by TC components: The sample was taken to near dryness with a stream of nitrogen, 1.0 ml saturated KOH in ethanol was added, and the solution was refluxed on a steam bath for 15 minutes. After cooling, 5.0 ml water and 1.0 ml hexane were added, the mixture was shaken and allowed to separate, and the hexane layer was analyzed by EC-GC. The two major TC peaks that coelute from silicic acid with PCB (Fig. 8) were eliminated by this procedure (Fig. 12).

Glass capillary chromatography

Glass capillary chromatography has greatly enhanced the resolution of multi-component air samples. Two 25-m OV-101 columns obtained from Varian Corporation (Walnut Creek, CA) deteriorated rapidly with use. The most common difficulty was a "beading up" of the stationary phase on the first few coils of the column. Small droplets of the stationary phase could be seen under a microscope. This loss of stationary phase from the glass surface, apparently caused by solvent injection, produced a severe loss in resolution. During the last two months of the project we used a Supelco SP-2100 AA grade column (30 m) and had excellent success. Injections of 5 μ l using the Grob technique (Grob and Grob, 1978) produced good resolution with no evident column deterioration.

Capillary analysis of PCB in Columbia air is exemplified by Figs. 13 and 14. These samples were extensively cleaned up before analysis: by alumina chromatography followed by silicic acid fractionation and by treatment with both alcoholic KOH and 7% fuming sulfuric acid. Although many of the peaks in the sample patterns match Aroclor fingerprints, the numerous major peaks that do not match are worthy of note, especially in the Aroclor 1016 region. The PCB analyses reported in Section 3 were done on packed columns, and the precision of replicate samples and the agreement between PCB levels determined using different adsorbents is good. However, the accuracy of Aroclor 1016 analysis by packed column GC is questionable because of the presence of underlying electron capturing compounds that do not appear to be PCB (despite removal of two major interferences from TC, see above). These results suggest that the Aroclor 1016 levels determined on packed columns may be up to twice those measured after better separation on a capillary column. One of the

TABLE 6. INTERFERENCE OF TECHNICAL CHLORDANE WITH AROCLOR 1016 DETERMINATION

TC:PCB	Silicic acid procedure ^b	% Error in PCB determination	
		SP-2250/SP-2401	OV-225
0.58	B	2	5
	AB	-1	6
1.17	B	15	8
	AB	9	23
1.75	B	21	40
	AB	28	43
2.23	B	18(?)	54
	AB	36	53
2.92	B	35	62
	AB	38	65

(a) Quantities of A-1016 and TC applied to the silicic acid columns were 4.56 and 2.66-13.3 μ g, respectively.

(b) B = Bidleman *et al.* (1978), AB = Armour and Burke (1970).

recommendations in Section 5 is that a careful scrutiny be done of apparent Aroclor 1016 levels determined by packed and capillary GC and that capillary chromatograms be systematically screened for low molecular weight PCB components using pattern recognition techniques.

A capillary chromatogram of the "toxaphene fraction" (silicic acid column fraction 4, Table 4) is shown in Figure 15. The later portion of the sample chromatogram matches the toxaphene standard fingerprint, but the peak height ratios are different, caused perhaps by selective volatilization or degradation of certain toxaphene components, or the presence of organochlorines which underlie toxaphene peaks. Also, the early portion of the chromatogram shows a great number of peaks that are probably not toxaphene components. On the basis of retention times we have tentatively identified two of these major peaks as α - and γ -hexachlorocyclohexane, organochlorines which coelute with toxaphene from the silicic acid column. The other peaks remain unidentified.

This chromatogram and those of PCB fractions (Figs. 13 and 14) illustrate the tremendous complexity of electron-capturing compounds found in urban air. Although we have no proof that all of these compounds are halogenated organics, most other electron-capturing molecules would probably be removed by the 7% fuming sulfuric acid treatment. Phthalate esters, for example, do not survive this treatment, and the oxygenated

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pesticides dieldrin and endrin are also removed. Certain oxygen-containing compounds do appear to resist acid treatment however. Veierov and Aharonson (1978) found that heptachlor epoxide was only partially removed by sulfuric acid treatment, and pentachloroanisole also appears to be stable (Sundström, 1979). Thus it is impossible to identify all the compounds responsible for the complex array of peaks in Figs. 13-15 without a detailed GC-MS analysis.

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SECTION 3

FIELD SAMPLING WITH PUF, TENAX-GC RESIN, AND XAD-2 RESIN

Replicate collections of airborne PCB and chlorinated pesticides were carried out in Columbia, SC over a 27-month period from May, 1977 to August, 1979. Sampling during 1977 was done with PUF alone; while in 1978-79 comparative collections were made by operating PUF and Tenax samplers over the same time period. A single run with all three adsorbents was made during the spring of 1979. Characteristics of solid adsorbents used in front and backup traps are given in Table 7. Initially, we also investigated Tenax in the 60/80 mesh size, but it proved so difficult to handle (a puff of wind blew it away) that all field work was done with the 35/60 mesh resin.

TABLE 7. WEIGHT AND CROSS-SECTIONAL AREA OF SOLID ADSORBENT COLLECTORS

<u>Adsorbent</u>	<u>Quantity, g</u>	<u>Area, cm²</u>	<u>Mesh Size</u>
PUF	7.9	42	---
Tenax-GC	10.0	54	35/60
XAD-2	20.0	54	20/50

For each experiment upper and lower adsorbent traps were analyzed to determine the extent of organochlorine breakthrough, and in a few early experiments the glass fiber filters were also analyzed. Collection and analytical procedures are described in Section 2-B and 2-C.

Very little PCB or chlordane was retained by the glass fiber filter in a 24-hour or longer sampling period, although on some days appreciable fractions of p,p'-DDT were filter-retained. Average percentages of filter-retained organochlorines in Columbia were: Aroclor 1016 < 2, Aroclor 1254 = 6, chlordane < 2, and p,p'-DDT = 17. Because of possible desorption of organochlorines from particles deposited on the filter, we hesitate to equate filter-retained organochlorines with "particulate" organochlorines, although it is evident that higher proportions of the less volatile materials are collected by the filter.

The collection characteristics of PUF, Tenax-GC, and XAD-2 are summarized in Table 8, where quantities of PCB and chlorinated pesticides found on the backup traps are expressed as a percentage of the front trap values. HCB was very poorly retained by PUF in all air volume ranges, as

can be seen by the nearly equal quantities of HCB found on the front and backup traps. Tenax-GC and XAD-2 were far more effective in retaining HCB, and the levels of HCB found in ambient air using these adsorbents were several times higher than HCB concentrations determined with PUF collection (Tables 9 and 14). The pellicular resins also appeared to have a slight advantage over PUF for collecting low molecular weight PCB, the difference being most noticeable at the higher air volumes. The Tenax and XAD-2 runs are not directly comparable because twice as much XAD-2 (20 g) as Tenax was used in both the upper and lower traps. This was done because we found it difficult to uniformly cover the cross sectional area of the sampler (Fig. 5) with only 10 g of the more dense XAD-2 resin. The apparent superiority of XAD-2 over Tenax for collecting HCB may thus simply be due to the greater weight of XAD-2 used.

Surprisingly, Tenax appeared to be slightly poorer than PUF for collecting the higher molecular weight organochlorines (Aroclor 1254, chlordan, toxaphene). The reason for this is not apparent. We speculate that a physical transfer of Tenax "fines" from the front to the backup trap through the 80-mesh screen may have contributed to the organochlorine content of the rear trap (the 35/60-mesh Tenax was not sieved before use). However losses to the backup trap amounted to 5% or less of the front trap quantities and for most purposes would be negligible.

Comparisons between PUF and Tenax-GC for collecting HCB, Aroclors 1016 and 1254, chlordan (*cis*- and *trans*- isomers), and toxaphene are given in Tables 9-13. In a number of experiments p,p'-DDT levels were so low that they could not be determined because of toxaphene interferences (despite silicic acid fractionation) and we have therefore not included p,p'-DDT values in the tables. On many occasions duplicate or triplicate samples were also taken with a single adsorbent system, allowing relative standard deviations to be determined. These precisions reflect both the variability in the sample collection and the analytical procedure.

The agreement between airborne organochlorine levels determined by PUF and Tenax-GC collection was very good except for HCB. Because of the poor retention of HCB by PUF, levels of HCB measured by Tenax collection were several times higher. Except for one experiment, levels of Aroclor 1016 determined by Tenax collection were slightly higher, probably a reflection of the slightly better Aroclor 1016 retention by Tenax (Table 8). The average difference between Aroclor 1016 values determined by the two methods was only 14%, however, even excluding the low result (Table 10). For Aroclor 1254, chlordan, and toxaphene the average difference between the PUF and Tenax values was less than 5%, with no trend toward high or low results with either adsorbent (Tables 11-13).

On May 19, 1979 comparative collections were made with PUF, Tenax, and XAD-2. Levels of Aroclor 1254, chlordan, and toxaphene determined by the three methods agreed excellently (Table 14). The Aroclor 1016 concentration measured with XAD-2 was higher than that found with PUF or Tenax. Breakthrough did not appear to be a problem during this experiment; percentages of Aroclor 1016 found on backup traps were 15% (PUF), 2% Tenax and <1% (XAD-2), and second-trap quantities were included in calculating

the Table 14 results. This suggests that the higher Aroclor 1016 value found using XAD-2 may have resulted from an analytical error, not from sample loss during collection. Support for this suggestion is given by the close agreement between HCB values determined by Tenax and XAD-2 collection. Nevertheless, further comparisons using all three collection systems simultaneously would be desirable.

Duplicates or triplicates using the same solid adsorbent generally agreed within 20%, although in a few cases one sample of a triplicate set was considerably different from the other two, resulting in much larger relative standard deviations (see Table 9, 3/17/79 Tenax; Table 10, 3/7/79 Tenax; and Table 11, 9/19/77 PUF). The fact that poor precisions on a given day were associated with an individual organochlorine and not with the five types of compounds collected indicated that analytical errors and not sampling problems were responsible. In one case the deviant result could be discarded from the other two by application of a q-test at the 90% confidence level, but with such a small data set we preferred not to do this and all data were retained in calculating the precisions on these dates.

TABLE 8. AVERAGE RELATIVE QUANTITIES OF ORGANOCHLORINES
ON BACKUP ADSORBENT TRAPS (FRONT TRAPS = 100)

m ³ Air	Adsorbent	Experiments	HCB	Aroclor 1016	Aroclor 1254	Chlordane	Toxaphene
300 ^a	PUF	5	55	10	< 1	< 1	< 1
500-750	PUF	14	96	10	< 3	< 1	< 1
	Tx	9	12	10	< 3	< 3	< 2
900-1200	PUF	3	106	24	2	< 1	< 1
	Tx	5	19	12	4	< 5	< 2
	XAD-2	1	1	< 1	< 1	< 1	< 1
1300-1650	PUF	5	84	30	2	< 1	3
	Tx	2	20	16	4	< 6	4

* Four of these experiments were carried out using 3 PUF plugs; average relative quantities of HCB and Aroclor 1016 on the third plug were 41 and 4, respectively.

Even including the few sets with relative standard deviations > 50%, the average relative standard deviations for each organochlorine ranged from 7.9-22% and were of the same magnitude as the analytical precisions (Table 5, Section 2-C). Thus the limiting factor in obtaining precise

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values for airborne organochlorines appears to be analytical, not sampling.

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TABLE 14. COMPARATIVE COLLECTION OF AIRBORNE ORGANOCHLORINES
WITH THREE SOLID ADSORBENTS¹

	<u>PUF mean of 2</u>	<u>Tenax mean of 2</u>	<u>XAD-2 single sample</u>
HCB	0.078	0.253	0.213
Aroclor 1016	1.76	2.24	3.14
Aroclor 1254	0.99	0.92	1.05
Chlordane	1.59	1.74	1.44
Toxaphene	3.23	3.72	3.68

¹Samples were collected May 19, 1979; air volumes were 912 m³ (PUF), 736 m³ (Tenax, and 903 m³ (XAD-2).

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TABLE 9. REPLICATE COLLECTIONS OF HEXACHLOROBENZENE (HCB) ON POLYURETHANE FOAM AND TENAX-GC RESIN

Collection date	Polyurethane foam (PUF)		Tenax-GC resin	
	$\bar{X}$, ng/m ³ (number of samples)	% rel. s.d.	$\bar{X}$, ng/m ³ (number of samples)	% rel. s.d.
5/9/77	0.112 (3)	6.2	0.403 (1)	+85.0
5/10/77	0.119 (3)	5.9	0.323 (1)	+73.1
6/9/77	0.060 (2)	3.3	0.311 (1)	+85.2
8/31/77	0.090 (3)	17.3	0.283 (1)	+86.9
9/19/77	0.150 (3)	4.6	0.257 (3)	+67.7
10/12/77	0.264 (2)	7.6	0.311 (3)	+72.3
12/23/77	0.210 (3)	23.0	0.253 (2)	+69.2
8/31/78	0.059 (1)		0.273 (3)	+94.1
9/6/78	0.087 (1)		0.287 (1)	+84.3
9/12/78	0.046 (1)		0.394 (1)	+81.0
9/14/78	0.037 (1)		0.310	+79.9
3/7/79	0.083 (2)	6.8		
3/17/79	0.086 (2)	1.6		
5/21/79	0.078 (2)	2.7		
7/14/79	0.016 (1)			
8/14/79	0.045 (1)			
8/22/79	0.075 (1)			
MEANS:	0.095	7.9		22.2

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TABLE 10. REPLICATE COLLECTIONS OF AROCLOR 1016 ON POLYURETHANE FOAM AND TENAX-GC RESIN

	Polyurethane foam (PUF)	Tenax-6C resin
Collection date	$\bar{X}$, ng/m ³ (number of samples) % rel. s.d.	$\bar{X}$, ng/m ³ (number of samples) % rel. s.d.
5/9/77	3.08 (3) 7.5	
5/10/77	3.12 (3) 4.8	
6/9/77	6.57 (2) 37.0	
8/31/77	10.0 (3) 16.2	
12/23/77	2.34 (3) 12.0	
8/31/78	5.29 (1)	
9/6/78	4.15 (1)	
9/12/78	4.18 (1)	
9/14/78	3.06 (1)	
3/7/79	1.64 (2) 23.3	
3/17/79	1.75 (1)	
5/21/79	1.76 (2) 0.3	
7/14/79	1.21 (1)	
8/14/79	2.61 (1)	
8/22/79	2.71 (1)	
MEANS:	3.56 14.4	3.14 21.6
		+7.0 +10.4 +1.2 +4.4 +10.9 +7.9 +21.4 +32.0 -26.7 +29.6 +9.8

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TABLE 11. REPLICATE COLLECTIONS OF AROCLOR 1254 ON POLYURETHANE FOAM AND TENAX-GC RESIN

Collection date	Polyurethane foam (PUF)		Tenax-GC resin	
	$\bar{X}$, ng/m ³ (number of samples)	% rel. s.d.	$\bar{X}$, ng/m ³ (number of samples)	% rel. s.d.
5/9/77	1.10 (3)	7.9		
5/10/77	0.84 (3)	13.7		
6/9/77	1.18 (2)	6.0		
8/31/77	3.68 (3)	16.0		
9/19/77	3.79 (3)	50.0		
10/12/77	1.23 (2)	3.3		
12/23/77	1.02 (3)	23.0		
8/31/78	2.59 (1)			
9/6/78	2.23 (1)			
9/12/78	2.34 (1)			
9/14/78	2.27 (1)			
3/7/79	0.56 (2)	4.0		
3/17/79	0.72 (1)			
5/21/79	1.00 (2)	0.8		
7/14/79	1.18 (1)			
8/14/79	1.09 (1)			
8/22/79	2.15 (1)			
MEANS:	1.70	13.9	1.58	12.3
			2.42 (1)	-7.0
			2.10 (1)	-6.2
			2.48 (1)	+5.6
			2.19 (1)	-3.7
			0.72 (3)	+22.0
			0.85 (3)	+14.4
			0.92 (2)	-8.7
			0.88 (3)	-34.1
			1.18 (1)	+7.6
			2.08 (1)	-3.4
			1.58	-1.3

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TABLE 12. REPLICATE COLLECTIONS OF CHLORDANE ON POLYURETHANE FOAM AND TENAX-GC RESIN

Collection date	Polyurethane foam (PUF)		Tenax-GC resin	
	$\bar{X}$, ng/m ³ (number of samples)	% rel. s.d.	$\bar{X}$, ng/m ³ (number of samples)	% rel. s.d.
5/9/77	0.357 (3)	7.6	0.793 (1)	-0.8
5/10/77	0.503 (3)	3.9	1.90 (1)	0.0
6/9/77	0.441 (2)	6.6	1.84 (1)	-6.0
8/31/77	2.13 (3)	12.0	2.69 (1)	-2.6
9/19/77	1.72 (3)	16.0	0.510 (3)	+21.6
10/12/77	1.23 (2)	3.3	0.426 (3)	+10.1
12/23/77	0.578 (3)	19.8	1.74 (2)	+8.6
8/31/78	0.799 (1)		1.45 (3)	+6.2
9/6/78	1.90 (1)		1.40 (1)	+5.0
9/12/78	1.95 (1)		2.55 (1)	-24.7
9/14/78	2.76 (1)		1.53	+1.7
3/7/79	0.400 (2)	6.7		
3/17/79	0.383 (2)	15.1		
5/21/79	1.59 (1)	2.8		
7/14/79	1.36 (1)			
8/14/79	1.33 (1)			
8/22/79	3.18 (1)			
MEANS:	1.33	9.4	14.2	8.1

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TABLE 13. REPLICATE COLLECTIONS OF TOXAPHENE ON POLYURETHANE FOAM AND TENAX-GC RESIN.

Collection date	Polyurethane foam (PUF)		Tenax-GC resin	
	$\bar{X}$, ng/m ³ (number of samples)	% rel. s.d.	$\bar{X}$, ng/m ³ (number of samples)	% rel. s.d.
5/9/77	0.444 (3)	17.0		
5/10/77	0.472 (3)	12.0		
6/9/77	1.19 (2)	10.0		
8/31/77	66.3 (3)	9.8		
9/19/77	1.72 (3)	16.0		
10/12/77	1.31 (2)	6.1		
12/23/77	3.08 (3)	4.0		
8/31/78	18.4 (1)		17.6 (1)	-4.7
9/6/78	26.0 (1)		26.4 (1)	+1.8
9/12/78	15.3 (1)		15.3 (1)	0.0
9/14/78	60.5 (1)		42.2 (1)	-43.3
3/7/79	1.01 (2)	16.6	1.58 (3)	+35.6
3/17/79	1.10 (2)	5.1	0.97 (3)	-13.4
5/21/79	3.23 (2)	3.1	3.72 (2)	+13.2
7/14/79	3.92 (1)		4.15 (3)	+5.5
8/14/79	19.7 (1)		20.3 (1)	+3.0
8/22/79	32.7 (1)		30.8 (1)	-6.2
MEANS:	15.1	10.0	16.3	-0.9
			11.5	

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SECTION 4

PCB VAPOR MOVEMENT THROUGH POLYURETHANE FOAM COLUMNS -- A LABORATORY STUDY

Collection efficiencies during field studies are normally determined by using a back-up trap. If the second trap contains substantially less material than the lead trap, complete collection is assumed. While this approach gives an indication of the collection efficiency under specific sampling conditions, it has limited predictive value. The experiments described in this section are aimed toward developing a general method for relating the movement of PCB isomers through PUF to volatility, flow rate, and total air volume.

A sampling cartridge filled with solid adsorbent behaves as a frontal gas-solid chromatography system, in which sample is continuously introduced to the column and subsequently moved through the column by the airflow. The collection efficiency of the trap is often characterized for low-volume systems by determining the "breakthrough volume" of air required to move the sample front through the column (Pellizzari et al., 1976; Melcher et al., 1978). This differs from elution chromatography, where the sample is introduced to the column as a single slug and then eluted as a band. Assuming linear adsorption isotherms, the retention volume for an elution experiment should be identical to the breakthrough volume for a frontal experiment, where breakthrough volume is taken as the point at which the concentration of solute in the column effluent is one-half the concentration introduced to the column (Pellizzari et al., 1976; Reilley et al., 1962). For reasons of experimental simplicity, we investigated PCB penetration through PUF by an elution chromatography system in order to determine the effects of total air volume and flow rate on PCB retention efficiency.

Our "high-volume gas chromatograph" is shown in Fig. 16 (Simon and Bidleman, 1979). Fourteen 1-cm thick PUF plugs were packed loosely into a 7-cm diameter x 25-cm long aluminum barrel. A fifteenth plug was spiked with about 40 µg of mixed PCB isomers (Analabs, Inc., North Haven, CT, Table 16) in hexane, the solvent was allowed to evaporate, and the spiked plug was placed at the front of the sampling train. A large PUF prefilter was placed over the entrance of the sampler to minimize contamination from organochlorines present in the laboratory atmosphere. Air was drawn through the foam column using a Rotron DR-313 brushless pump (Rotron Corp., Woodstock, NY) at flow rates of 0.15-0.81 m³/min and total air volumes of 300-1600 m³. Flows were controlled by placing a restrictor plate at the entrance to the foam column and were monitored during each experiment by measuring the pressure drop across the foam column with a Magnehelic gauge. The relationship between flow rate and pressure drop

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TABLE 15. CONCENTRATIONS OF PCB IN URBAN AIR

10^{-9} g/m^3

Aroclor 1016 Aroclor 1254 Total PCB
or 1242

Location	Dates	Samples		Aroclor 1016		Aroclor 1254		Total PCB		Reference
		Range	Mean	Range	Mean	Range	Mean	Range	Mean	
Columbia, SC	1977-79	14	1.2-10.0	3.6	0.6-3.8	1.7	5.3	1.8-13.8	5.3	This work
Chicago, IL	1975-76	4	6.7			1.3	8.0		8.0	Murphy and Rzeszutko, 1977
Milwaukee, WI	1977-78	8						0.07-2.3		Doskey, 1978
LaJolla, CA	1973	5			0.5-14	4.4				McClure, 1976
Jacksonville, FL	1975	13					8.8 ¹	4-36 ¹	8.8 ¹	Stratton et al., 1978
Gainesville, FL	1977	6					30 ¹	11-44 ¹	30 ¹	Stratton et al., 1978
Boston, MA	1978	1		5.3		3.3	8.8		8.8	Bidleman, unpublished
Providence, RI	1973	1					9.4		9.4	Bidleman and Olney, 1974b
Kingston, RI	1973	3					4.0		4.0	Bidleman and Olney, 1974b
Research Triangle Park, NC	1977	1		4		9	13		13	MacLeod, 1979

¹ Calculate as decachlorobiphenyl, values calculated as Aroclor 1242 would be about half these concentrations.

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was determined by using a Roots positive displacement calibrator. All experiments were carried out indoors at 23-26°C.

Since increased collection efficiency of organochlorine pesticides from water using silicone oil-coated PUF has been reported (Uthe et al., 1972), two tests were also carried out with PUF plugs that were coated with silicone oil. The plugs were dipped into a 0.5% solution of SE-30 or DC-200 chromatographic grade oils in petroleum ether and allowed to air-dry before use.

Individual PUF plugs were Soxhlet extracted with pesticide quality petroleum ether and the extracts were cleaned up by shaking with 7% fuming sulfuric acid. Analyses were carried out by electron capture gas chromatography on 1.5% OV-17/1.95% OV-210 or 3% OV-225 columns. The quantity of each PCB isomer found on the individual foam plugs was calculated and expressed as a percentage of the total isomer recovered. Recoveries of the total quantity of isomer applied to the spike plug ranged from 76-95% for experiments in which no apparent breakthrough occurred. The lowest recovery (76%) was for 3,3'-dichlorobiphenyl, and was traced to analytical losses in the extraction and concentration steps.

Studies of PCB movement through foam columns are complicated by the lack of uniformity and the fragile nature of PUF. Viewed under a microscope, PUF showed a generally open-pore structure, with thin films of polyurethane forming the pore walls and occasionally sealing off pores. Airflow resistance (as determined by the pressure drop across individual PUF plugs) varied by as much as 30% for plugs cut from the same section of stock foam. This variability was also reported by Turner and Glotfelty (1977), who selected plugs for their work by measuring the pressure drop under high-volume airflow. Plugs which had been reused many times appeared to be less efficient in retaining PCB than new plugs, and the variability seen in Figs. 20 and 21 is to a large extent the result of working with plugs that had been used up to 12 times for successive runs.

Individual PCB isomers were eluted through the PUF column in distinct bands and in order of decreasing volatility. The order of elution of the components of the commercial PCB mixture Aroclor 1016 through PUF paralleled their order of elution from a gas chromatographic column (Fig. 17). The greater penetration of 3,3'-DCB through PUF compared to the less volatile trichlorobiphenyls can be clearly seen in Fig. 18. Heavier PCB isomers (tetra-, penta-, and hexachlorobiphenyls) were also eluted in order of volatility (as indicated by molecular weight) (Fig. 19). These isomers were so effectively retained by PUF, even for air volumes exceeding 1600 m³, that most of our studies were concentrated on the lower isomers.

The penetration of PCB isomers (positions of their peak maxima) was linear with total air volume (Figs. 20 and 21). Retention volumes for the 15-cm PUF column, obtained by extrapolation of Figs. 20 and 21, were 1250 and 2700 m³ air for 3,3'-DCB and 2,4',5-TCB, respectively.

PUF plugs coated with silicone oils have been reported to be more effective in scavenging CHC pesticides from water than were uncoated plugs

(Uthe et al., 1972). This did not seem to be the case for air sampling, however. Peak elution characteristics for PCB through oil-coated plugs were indistinguishable from those obtained using uncoated foam (Figs. 20 and 21).

The collection efficiency of a PUF trap thus depends strongly on sample volatility and on the total volume of air passed through the collector. Initially, we thought that flow rate would also be an important factor in PCB retention. However, little difference was actually observed in the thickness of foam needed to retain a given percentage of the PCB at the highest and lowest flow rates tested, despite the fact that elution band widths increased with flow rate (Fig. 22). A recent field study (Stratton et al., 1978) has also found that the collection efficiency of PCB vapors of PUF was not flow-dependent within the range of flow rates attainable by most high-volume sampling equipment.

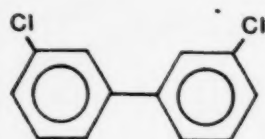
Table 17 summarizes the results of this PCB elution study by showing the thickness of PUF needed to retain 90% of the low molecular weight PCB (di- and trichlorobiphenyls) for 300, 600, and 900 m³ air sampled at flow rates ranging from 0.2 - 0.8 m³/min. These values were obtained by determining for each experiment the thickness of foam which included 90% of the area under a PCB isomer elution band (e.g., plug 11 for 3,3'-DCB in Fig. 18 and averaging the results for all experiments at each total air volume. For a frontal experiment, PCB would be continually introduced to the collector as well as being moved through the column, and the percentage of sample lost by breakthrough would be even less than that predicted by elution chromatography for the same air volume (Cropper and Kaminsky, 1963). Thus the values in Table 17 represent conservative estimates of the PUF thickness needed to retain PCB effectively. Two 7.6-cm diameter x 7.6-cm thick PUF plugs is a sufficient trap to retain PCB with molecular weights as low as dichlorobiphenyl in a 24-hour sampling period (600 m³ air). This includes all the components of Aroclor 1242 save a single monochlorobiphenyl isomer, which accounts for only about 1% of the commercial mixture (Webb and McCall, 1972).

TABLE 17. THICKNESS OF PUF NEEDED TO RETAIN 90% PCB

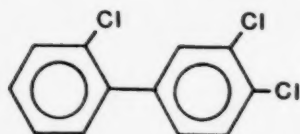
m ³ air	cm PUF ¹	
	3,3'-DCB	2,4'-5-TCB
300	7.3	4.4
600	11.3	6.1
900	>15	8.0

¹7.6-cm diameter plug

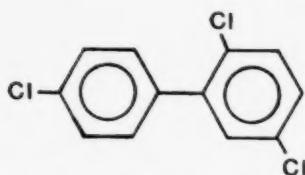
TABLE 16. PCB: ISOMERS USED IN ELUTION STUDY



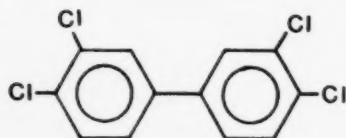
3,3'-DCB



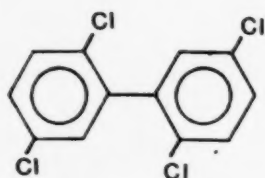
2,3,4-TCB



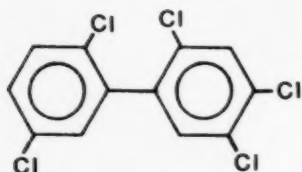
2,4,5-TCB



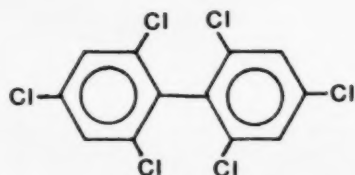
3,3',4,4'-TCB



2,2',5,5'-TCB



2,2',4,5,5'-PCB



2,2',4,4',6,6'-HCB

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CONCLUSIONS AND RECOMMENDATIONS

Selection of solid adsorbents for sampling

In choosing adsorbents for field work a number of considerations are important. Among these are: 1) level of background contamination in the adsorbent (the "blank"), 2) cost and reuseability of the adsorbent, 3) collection efficiency, and 4) ease of handling.

With careful cleanup all three of the tested adsorbents (PUF, Tenax-GC, and XAD-2) gave low background levels of organochlorines compared to what might be collected in a 24-hour sampling period, although the blanks for Tenax and XAD-2 were slightly higher than those for PUF. An important factor in limiting the blank value may be how carefully the adsorbents are protected from contamination after cleanup. MacLeod (1979) found that PCB levels in indoor air (houses, offices and laboratories) were much higher than concentrations in ambient air. We highly recommend that adsorbents be dried in vacuo after solvent extraction cleanup and that they be stored in tightly sealed containers.

PUF plugs have been reused successfully several times for air sampling with no apparent carryover of material between runs. Laboratory studies with thin sections of foam suggest that the retention efficiency of the foam decreases with use, however, probably because of mechanical tearing of the thin films of polyurethane which make up the cell walls (see Section 4).

While PUF is cheap and could be discarded after one of two uses if necessary, Tenax is considerably more expensive (\$90/15 g). Within two of our 10-g Tenax traps is contained over \$100 worth of adsorbent. It is thus very important to determine whether Tenax is effective for multiple uses. We have re-extracted Tenax after it has been used for air sampling and redried, and have observed that the extract is considerably more yellow than the extract of unused Tenax. Used Tenax also has a yellow color. Treatment of the extract with fuming sulfuric acid removes the yellow color, and we have not observed an increase in the blank for used Tenax by EC-GC. We are nevertheless concerned that the yellow color of the used Tenax and its extract indicates a breakdown of the resin. To determine the influences of repeated uses on Tenax stability, we recommend that a series of samples be collected in urban air and clean air (at a remote site) with new Tenax and resin that has been reused several times. For each experiment the collection efficiency (as determined by breakthrough of organochlorines into a second trap) and the blank value for Tenax batches that have been reused a number of times should be evaluated. Photomicrographs should be taken of the resin to visually determine if

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breakdown of the resin beads takes place with use.

All three solid adsorbents tested (PUF, Tenax-GC, and XAD-2) showed excellent collection efficiency for high molecular weight PCB (Aroclor 1254) and chlorinated pesticides under field conditions. Tenax resin showed a slight superiority for collecting light PCB (Aroclor 1016). Side-by-side collections of Aroclor 1016 with PUF and Tenax in the city of Columbia showed that on the average the Tenax traps collected 14% more of the light PCB mixture. Tenax was much more effective than PUF for collecting HCB. A single trial with XAD-2 suggested that this adsorbent was also very effective for trapping HCB and Aroclor 1016 at high air volumes, and we recommend that further studies be carried out with XAD-2.

The work described in this report was done in the city of Columbia, a city with no heavy industry. The air in Columbia is relatively clean and levels of organochlorine pesticides often are greater than PCB concentrations. Further testing of PUF, Tenax and XAD-2 should be carried out in highly industrialized cities and in rural areas. Experiments in cities with highly polluted air are important to determine (a) the stability of an adsorbent to breakdown under continued use, (b) the influence of other components of polluted air on the collection efficiency of adsorbents for organochlorines ("displacement effect") and (c) the collection efficiency of adsorbents for PCB vapors at high concentrations. Parallel experiments should also be done in rural areas, preferably with low concentrations of PCB, pesticides and other organics. Since the collection efficiency depends on the volatility of the organics, experiments should also be carried out under extremes of temperature; for example, by sampling in a northern city in the winter and a southern city during the summer.

By far the easiest material to handle in the field is PUF. The pellicular resins must be uniformly spread in the traps (Fig. 5) and care must be taken not to tilt the sampler during collection. A better design in which the pellicular adsorbents were held immobile in a cartridge would alleviate this problem.

Processes of vapor movement through solid adsorbents

Our work (Section IVC) demonstrated that PCB vapors move through a PUF column linearly with total air volume, and that the collection efficiency of a solid adsorbent system is thus limited by a "chromatography effect". The experiments in Section IVC were done by an elution system, in which a spike of PCB was placed at the head of the PUF column and eluted with clean air. The conclusions from this experiment should be applicable to a frontal, high-volume, collection system, for the retention volume for an elution experiment should be identical to the breakthrough volume for a frontal experiment (Reilley *et al.*, 1962). Experimentally this needs to be demonstrated however, and we recommend that vapor penetration experiments be extended to the actual determination of breakthrough volumes using a frontal system. At the same time the effect of temperature on organochlorine vapor penetration should be investigated, as Vidal-Madjar *et al.* (1978) found that for an elution experiment log retention volume was linearly related to the reciprocal of absolute

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temperature (for adsorption of chloroalkanes on Tenax and other solid adsorbents). A similar study carried out under high-volume conditions would elucidate the effect of ambient temperature on organochlorine breakthrough.

Analytical methods for airborne organochlorines

The complexity of halogenated organics in Columbia air is abundantly illustrated in Figs. 7, 9, 13, 14, and 15. Despite extensive fractionation of samples prior to GC analysis, uncertainty still remains in the identification of the multicomponent pollutants PCB and toxaphene. Capillary GC (Figs. 13 and 14) indicates that many of the compounds which coelute with PCB in silicic acid fractionation procedures and which would be identified as PCB on packed GC columns may in fact not be components of commercial Aroclors. A tremendous number of electron-capturing compounds which elute from capillary GC columns ahead of toxaphene remain unidentified (Fig. 15). It is clear that electron-capture GC alone, even using capillary columns, is insufficient to reliably identify the halogenated organics in the atmosphere.

We recommend that a heavy emphasis be placed on developing the analytical chemistry of airborne halogenated organics. Specific projects that would greatly further our knowledge in this area are:

1. A few air sample extracts taken in representative urban and rural areas of the U.S. should be subjected to intense scrutiny by GC-MS. Heavily industrialized and high pesticide use areas should be included. Sufficient sample should be collected at each site to permit reliable identifications, perhaps by pooling extracts of samples collected over a 1-2 week period at each location. This study, while far too time-consuming to carry out on a routine basis for air monitoring, would represent the first complete analysis of halogenated organics in air and may elucidate heretofore unidentified industrial organics as well as pesticide photoalteration products.

2. Intercalibration exercises should be carried out among investigators who are measuring organochlorines in air and rainfall. These studies should include (a) distribution of synthetic mixtures containing the halogenated organics identified in air, (b) distribution of portions of pooled air sample extracts, and (3) an intercomparison of sampling methodologies in which investigators convene for "sample-ins" at selected urban and rural locations.

3. Studies should be carried out to determine how multicomponent organochlorines (e.g., PCB, chlordane, toxaphene) are fractionated during evaporation into the atmosphere. The beginnings of such a study for toxaphene has been recently reported (Seiber *et al.*, 1979), and an enrichment of the more volatile toxaphene components upon evaporation from cotton foliage was noted. GC "fingerprints" of PCB and toxaphene in air samples are often different from those of analytical standards, presumably because of this selective evaporation of the lighter components (and also to the presence of interferences). It would seem that computer

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pattern recognition techniques could be used to match environmental sample chromatograms against artificially "weathered" standards. A computer approach to PCB pattern matching has been developed by Zobel (1974) and was recently applied to PCB in soil samples from Everglades National Park (Requejo et al., 1979).

4. Atmospheric removal processes, such as rainfall and dry deposition, should be investigated for organochlorines. These studies are important not only to determine fluxes of pollutants to earth, but also because selective atmospheric removal can change the distribution of compounds in a multicomponent mixture. We have found, for example, that dry deposition and rainfall removes Aroclor 1254 more rapidly than Aroclor 1016 and p,p'-DDT more rapidly than cis- and trans-chlordane, presumably because the less volatile organochlorines are preferentially adsorbed onto aerosols and deposited (Bidleman and Christensen, 1979).

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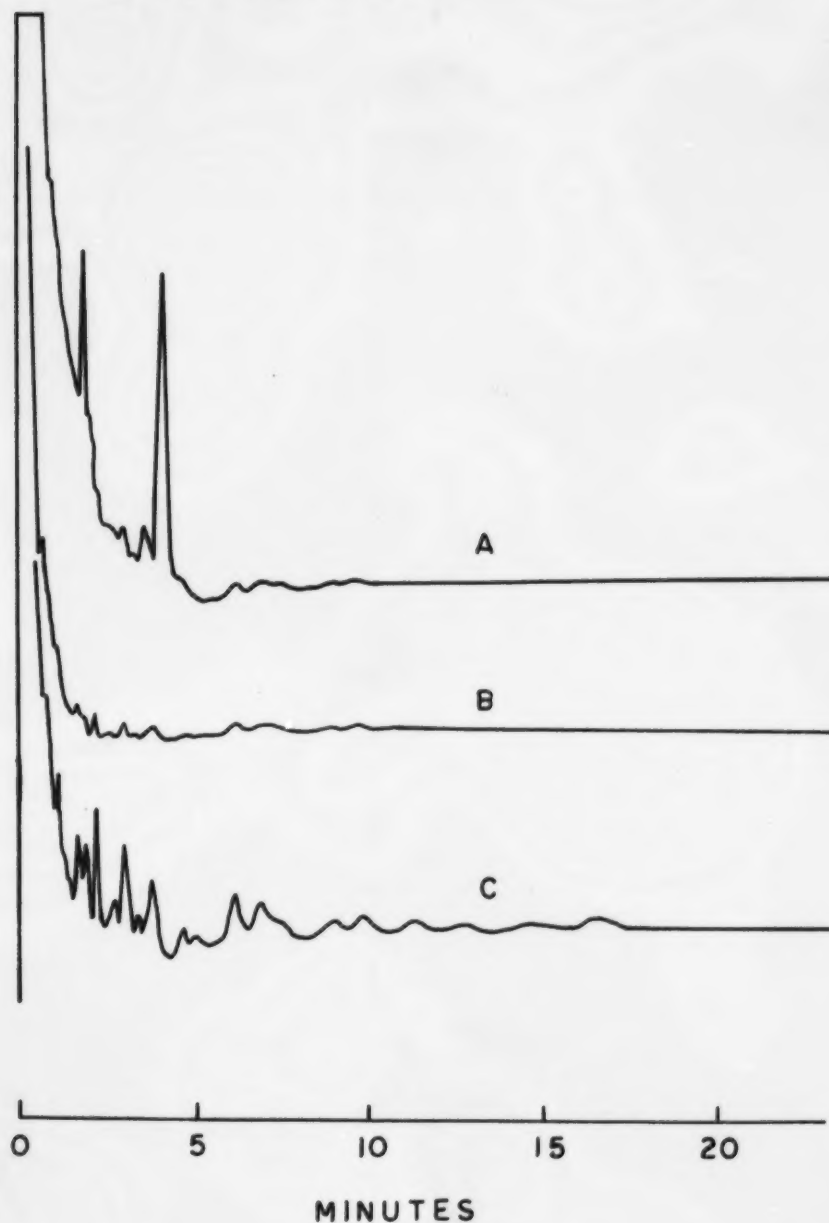
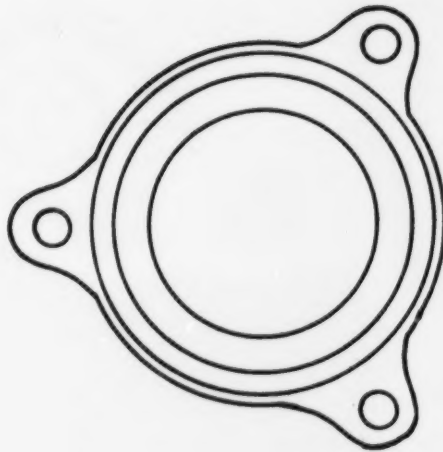


Figure 1. Chromatograms (1.5% SP-2250/1.95% SP-2401) of:
A. Foam plug extract, 10 μ l injection, 5.0-ml volume,
no cleanup. B. After alumina cleanup, 10 μ l injection,
5.0-ml volume. C. After alumina cleanup, 10 μ l injection,
1.0-ml volume.

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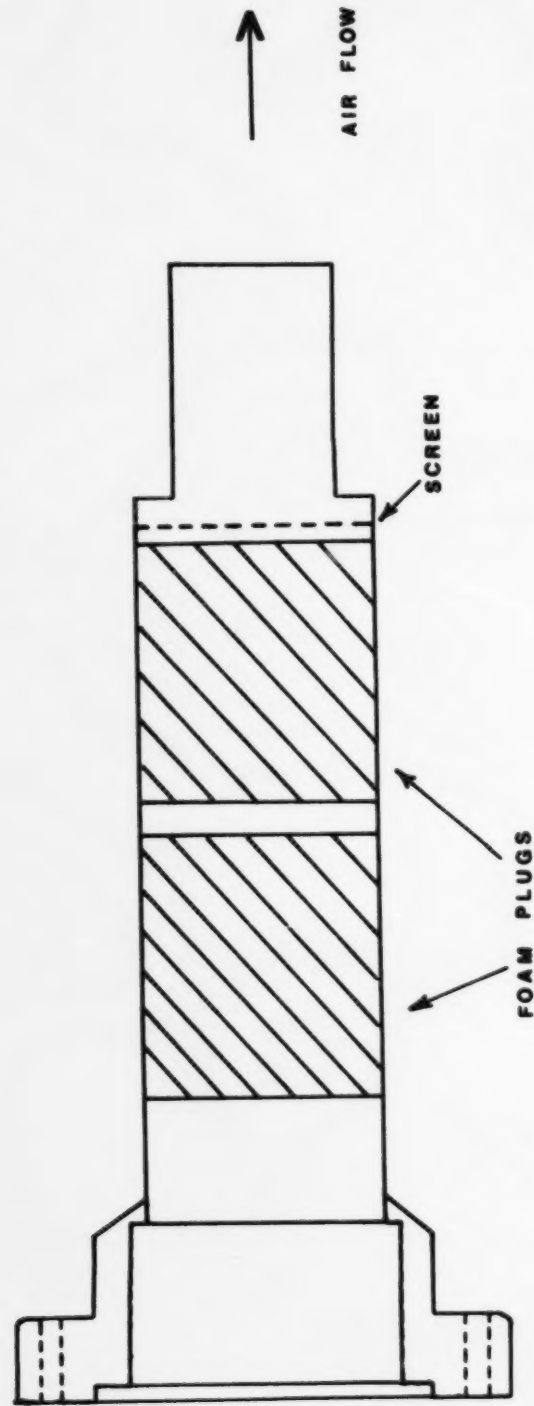
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Figure 2. Collection unit to hold a 10-cm diameter glass fiber filter and two PUF plugs, drawn approximately half scale. The wire screen to support the filter and the front retainer ring and rubber gasket are not shown.

GLASS FIBER FILTER

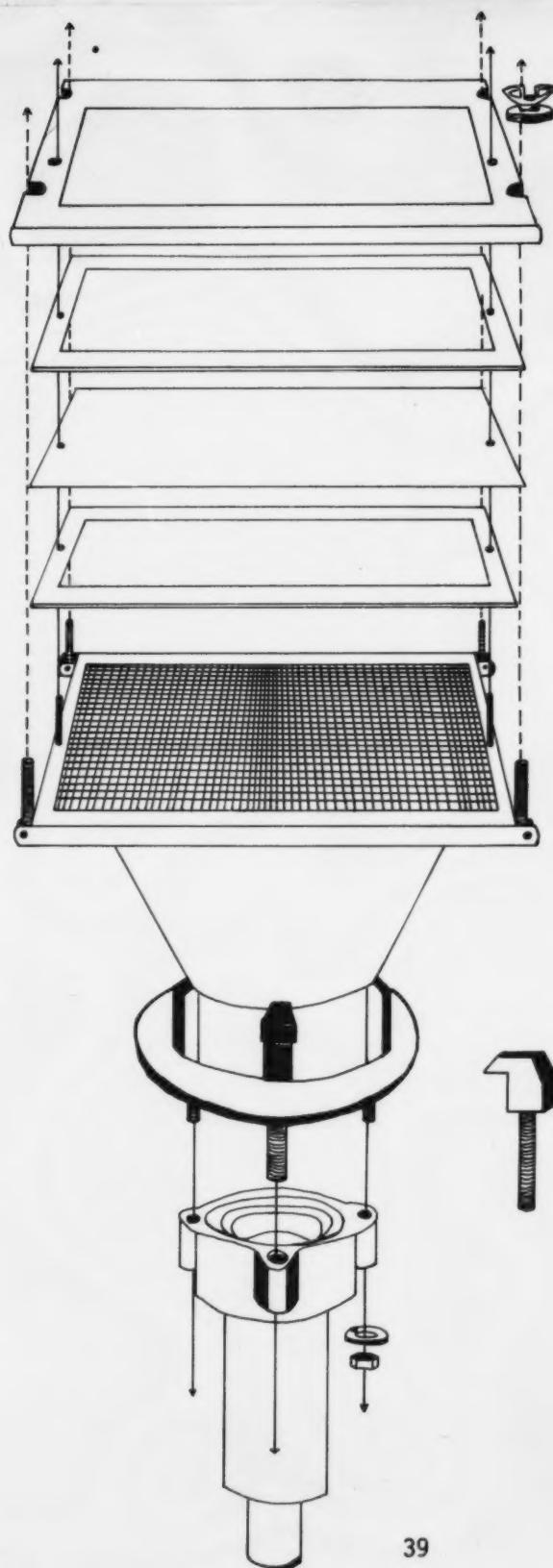


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Figure 3. Triplicate air samples taken atop the Physical Sciences Center with a PUF cartridge preceded by a 10-cm diameter glass fiber filter. Rain shields were made from cooking pots.

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Figure 4. PUF collection unit, showing attachment to a 20 x 25-cm filter holder.

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TENAX AND XAD-2 RESIN CARTRIDGE

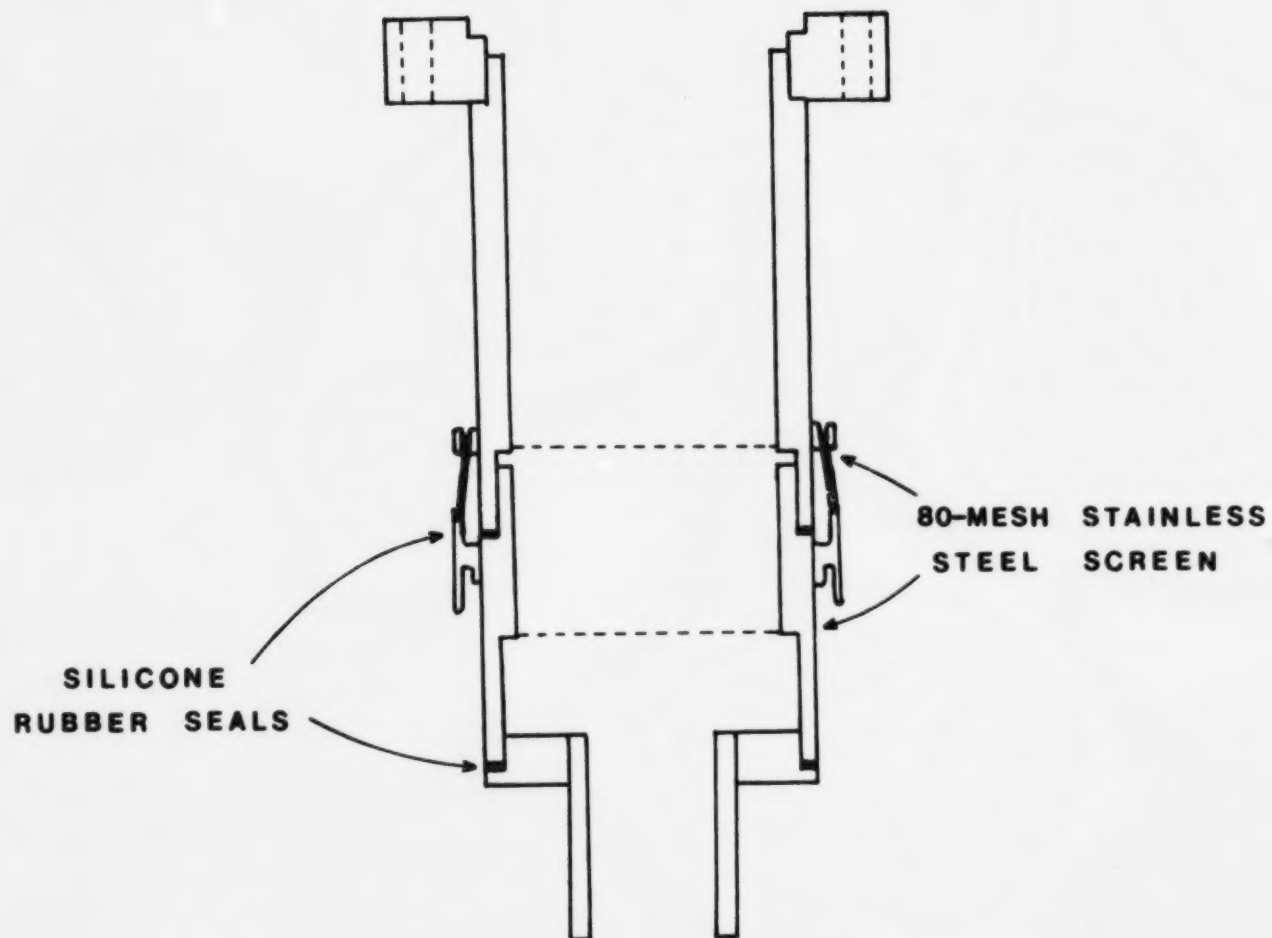


Figure 5. Collection unit to contain Tenax-GC or XAD-2 resin,
drawn approximately half scale.

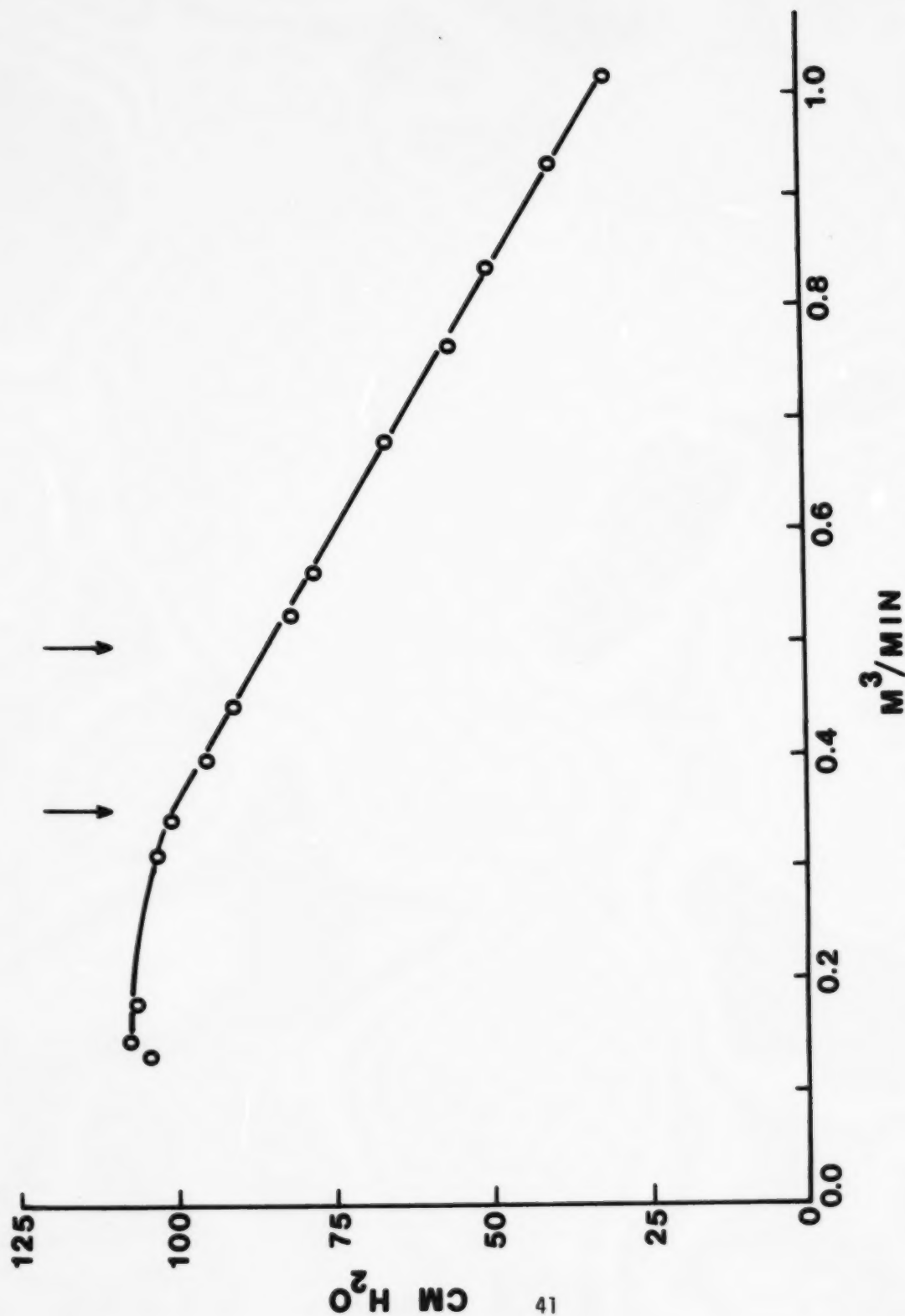
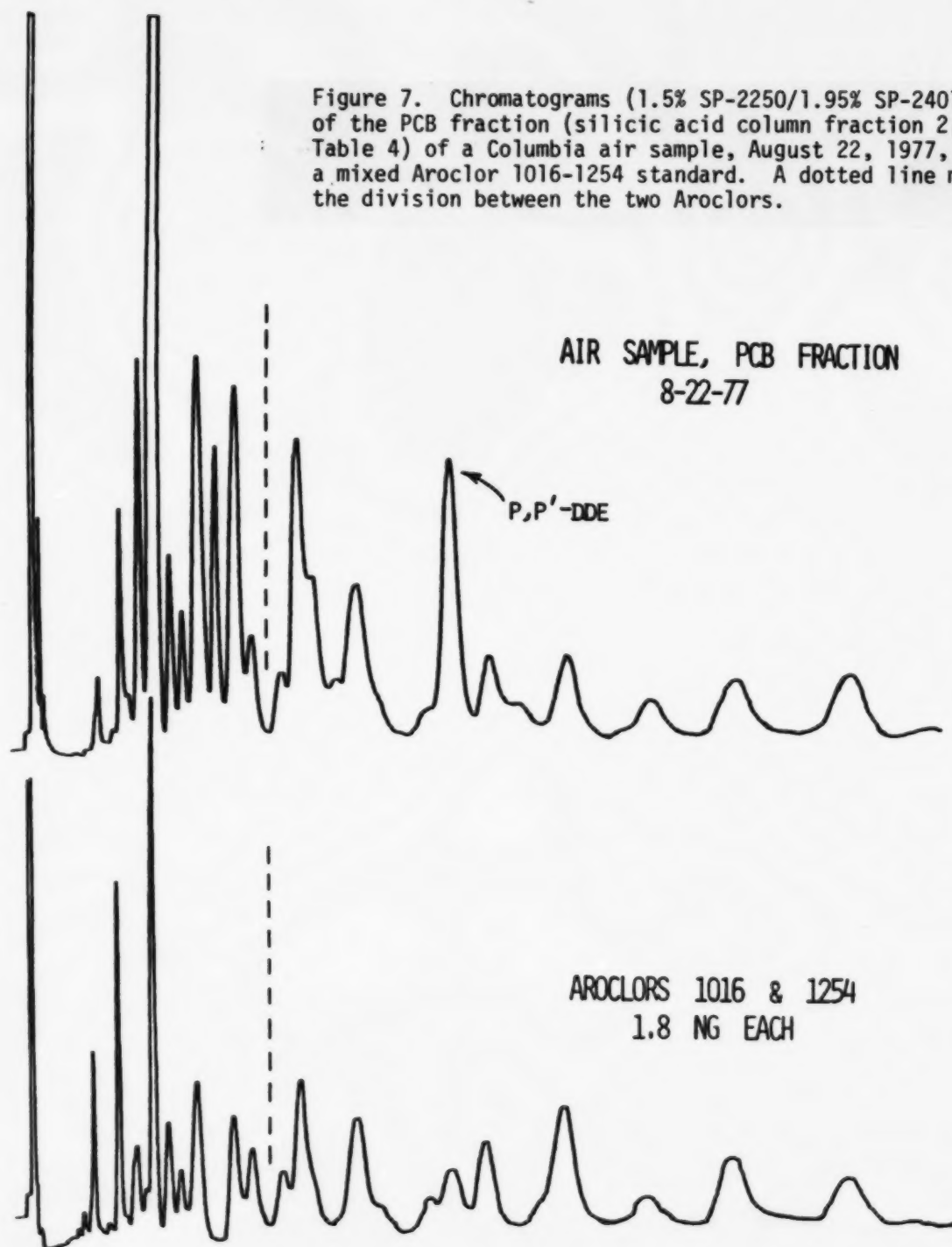


Figure 6. Calibration curve for Rotron DR-313 pump. Arrows indicate the range of flow rates obtained with solid adsorbent sampling cartridges.

Figure 7. Chromatograms (1.5% SP-2250/1.95% SP-2401) of the PCB fraction (silicic acid column fraction 2, Table 4) of a Columbia air sample, August 22, 1977, and a mixed Aroclor 1016-1254 standard. A dotted line marks the division between the two Aroclors.



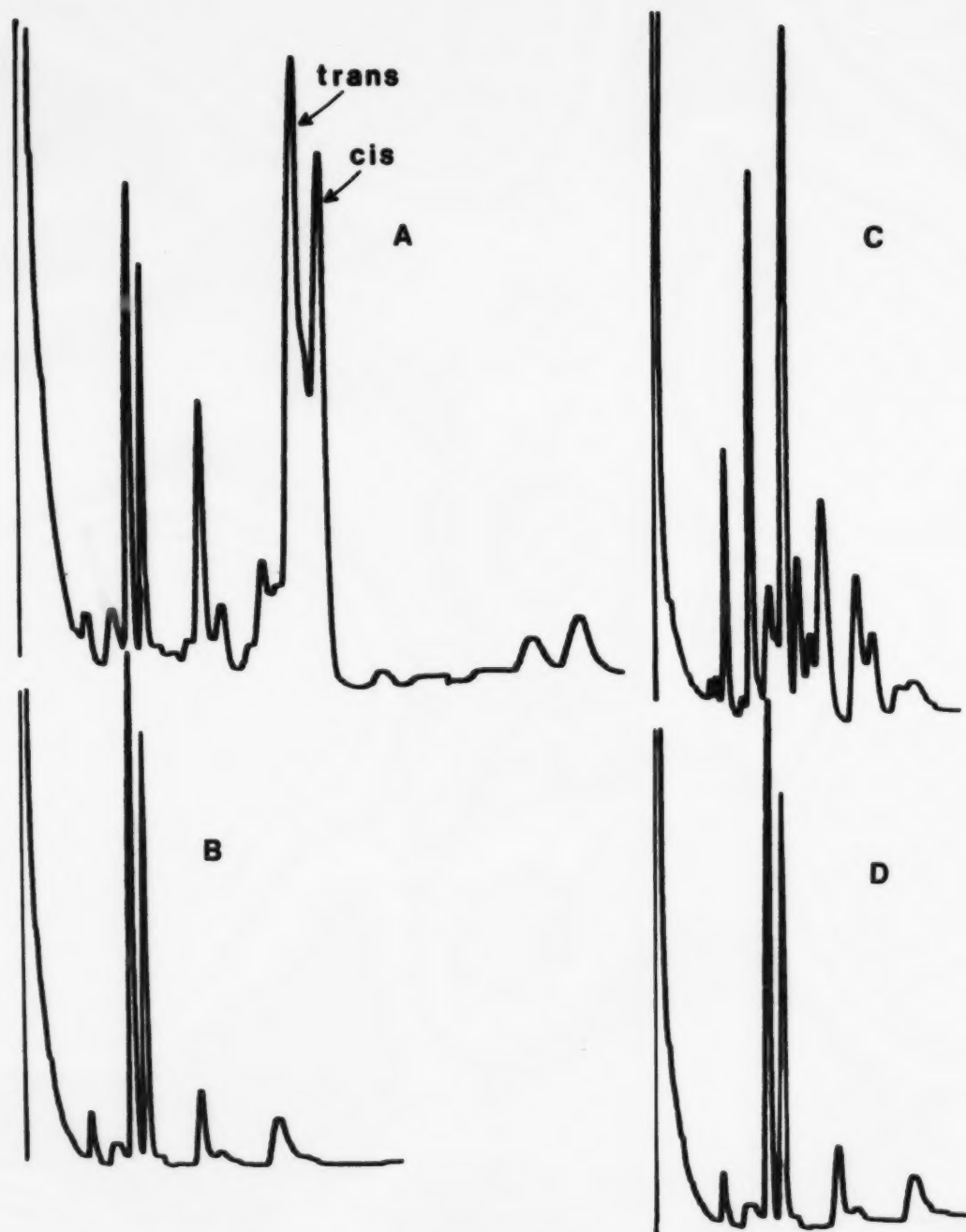


Figure 8. Chromatograms (1.5% SP-2250/1.95% SP-2401) showing relationships between: A. Technical chlordane, unfractionated. B and D. Technical chlordane components which coelute with PCB from a silicic acid column. C. Aroclor 1016.

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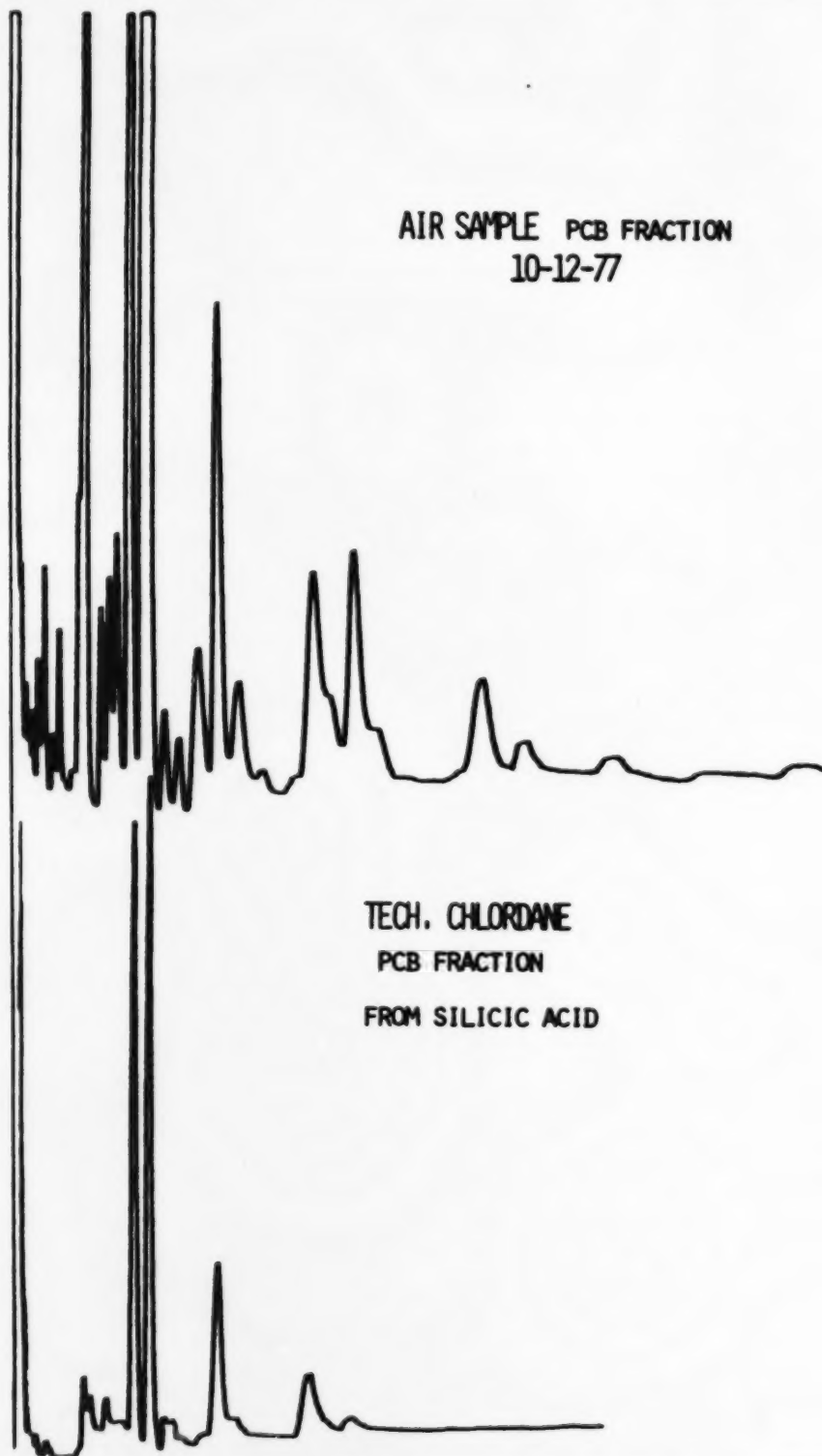
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Figure 9. Interference of technical chlordane components with Aroclor 1016 determination. Chromatograms (1.5% SP-2250/1.95% SP-2401) of PCB fractions (silicic acid column fraction 2, Table 4) of a Columbia air sample, October 12, 1977, and a TC standard.



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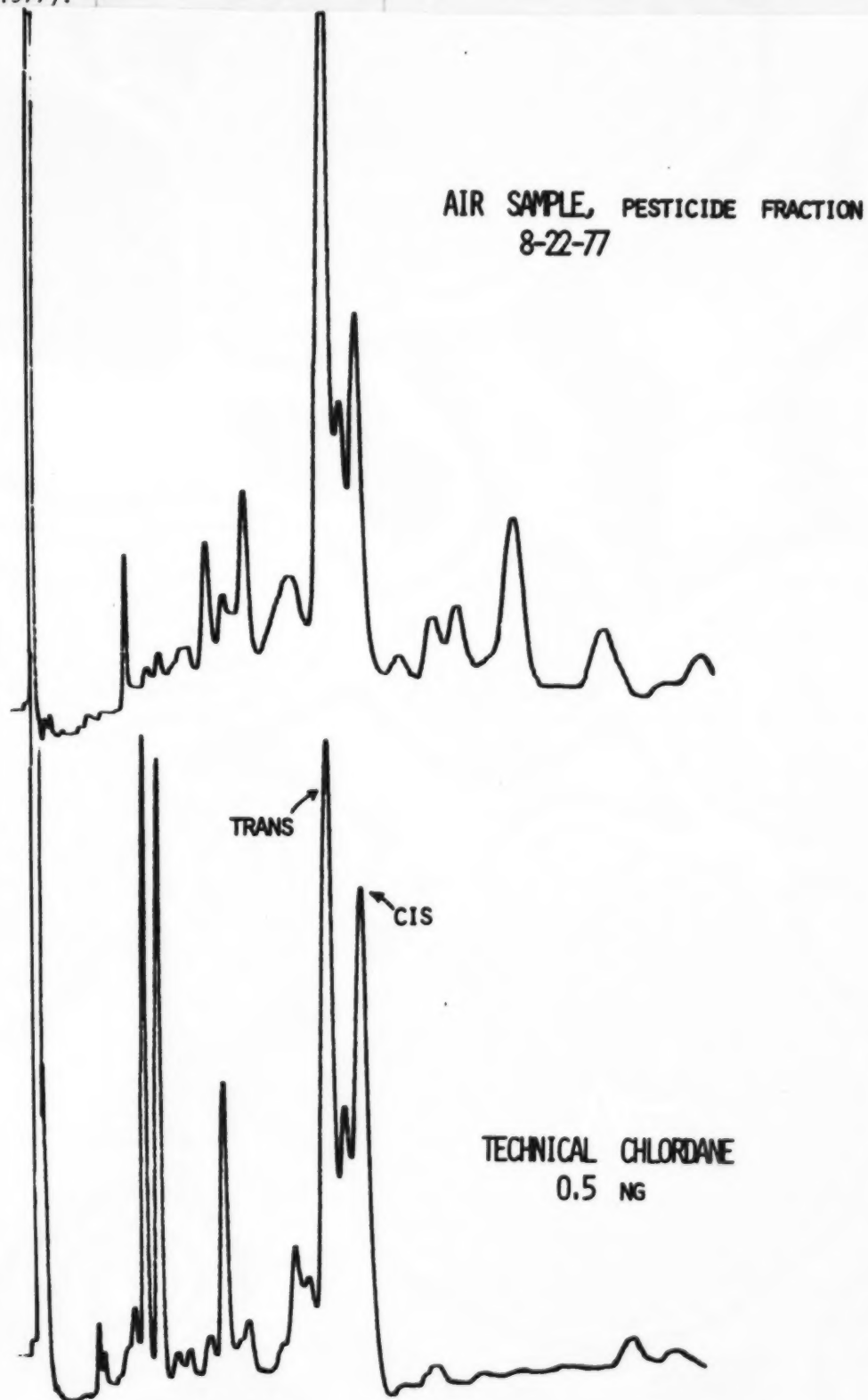
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Figure 10. Chromatograms (1.5% SP-2250/1.95% SP-2401) of the pesticide fraction (silicic acid column fraction 2, Table 4) of a Columbia, SC air sample, August 22, 1977 and a technical chlordane standard. The small peak between cis- and trans-chlordane is probably a nonachlor isomer (Sovocool et al., 1977).



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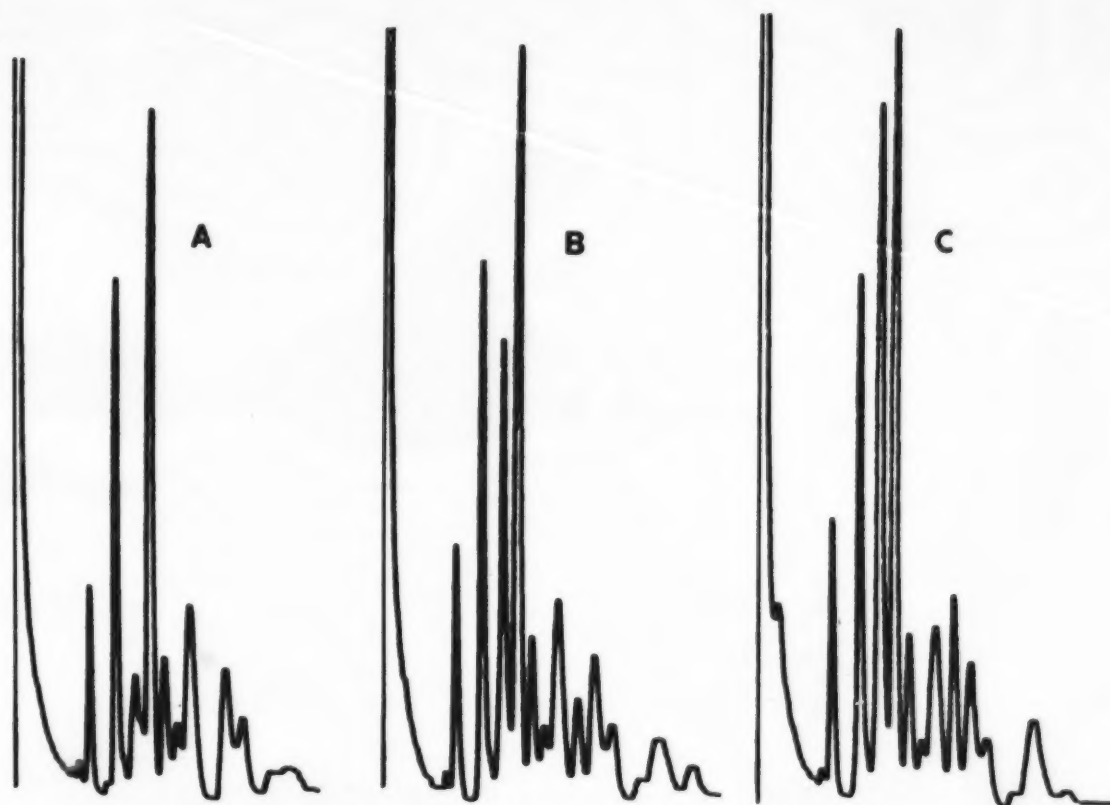
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Figure 11. Chromatograms (1.5% SP-2250/1.95% SP-2401) of TC-Aroclor 1016 mixtures after silicic acid fractionation. A. Aroclor 1016, no TC present B. TC:Aroclor 1016- 1.2. C. TC:Aroclor 1016 = 2.2.



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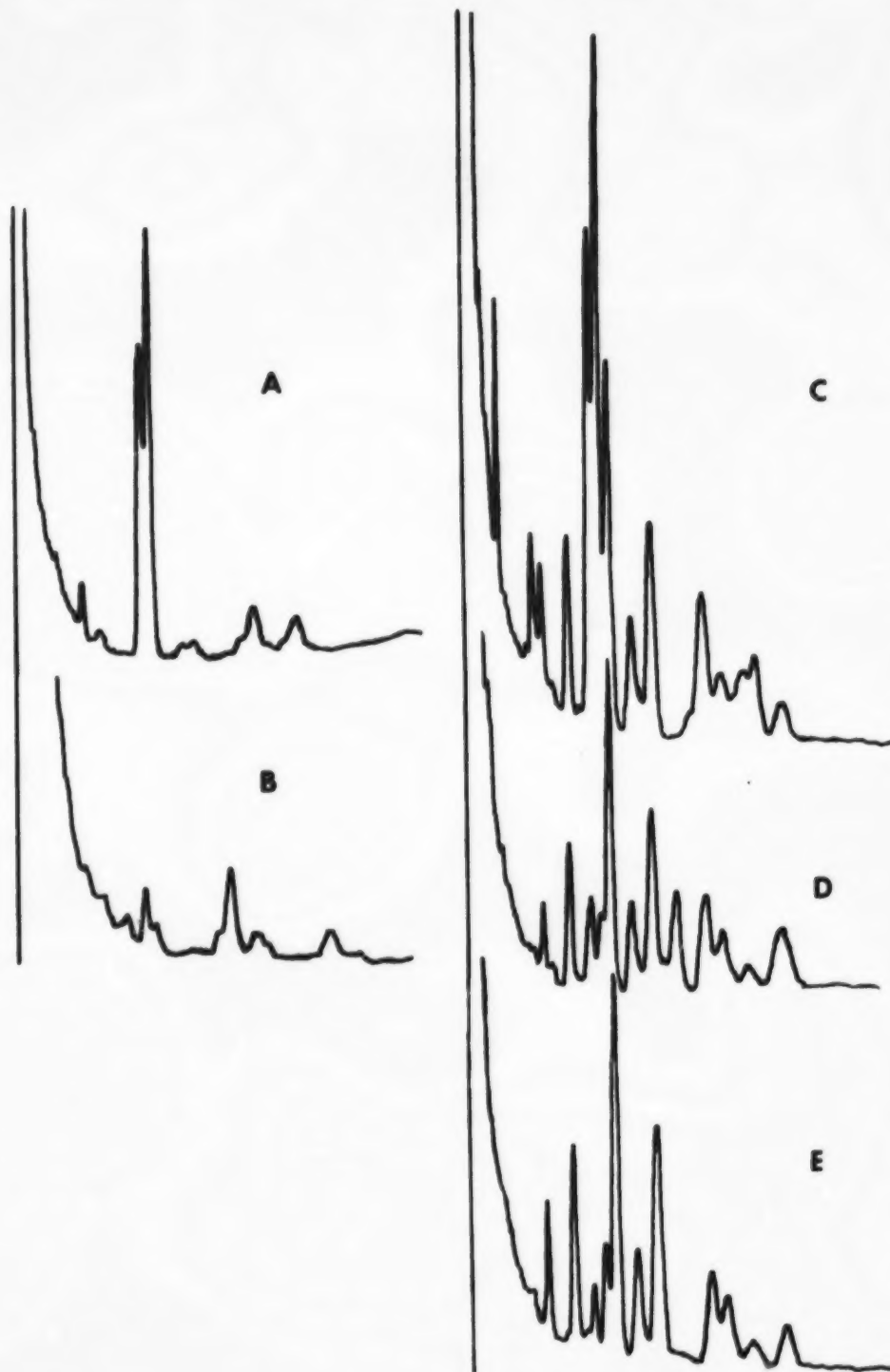
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Figure 12. Removal of TC interferences with Aroclor 1016 determination by alcoholic KOH treatment. Chromatograms (4% SE-30/6% SP-2401) of: A. TC, PCB fraction from silicic acid (Table 4). B. Same as A, after KOH treatment. C. TC-Aroclor 1016 mixture (TC:PCB = 2.3), PCB fraction from silicic acid. D. Same as C, after KOH treatment. E. Aroclor 1016 standard.



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Figure 13

Glass capillary chromatograms of the PCB fraction (silicic acid fraction 2, Table 4) of Columbia, SC air samples (Sept. 14, 1978) collected with PUF and Tenax-GC resin. The entire Aroclor 1016 and the early portion of the Aroclor 1254 pattern are shown with the division between the two Aroclors indicated by a dotted line. Sample peaks matching the PCB pattern are marked with an asterisk (shown for the PUF sample only). The large peak in the Aroclor 1254 portion of the sample chromatograms was identified by retention time as p,p'-DDE.

25-m OV-101 column, 200⁰ isothermal, 200 : 1 split injection.

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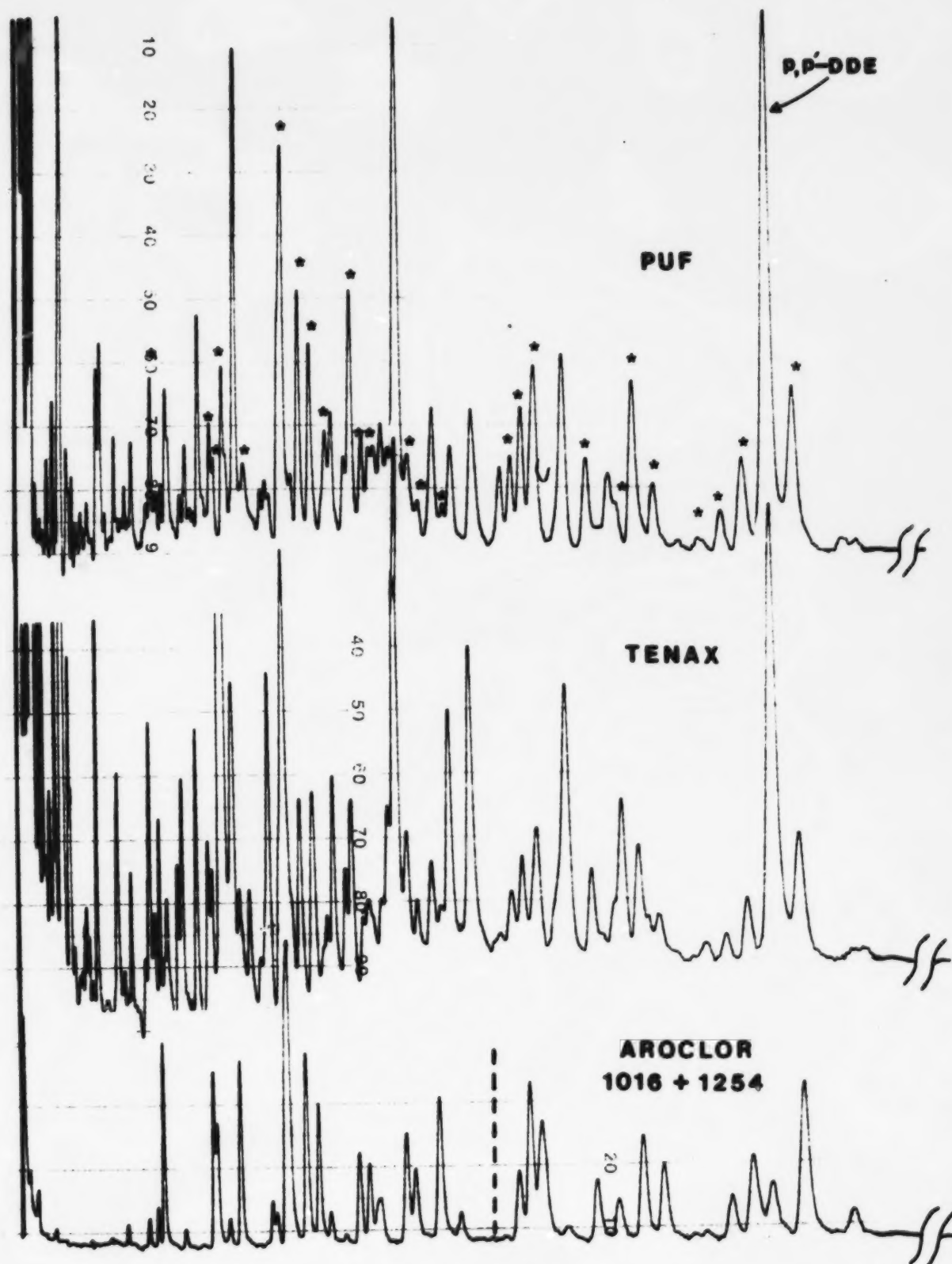
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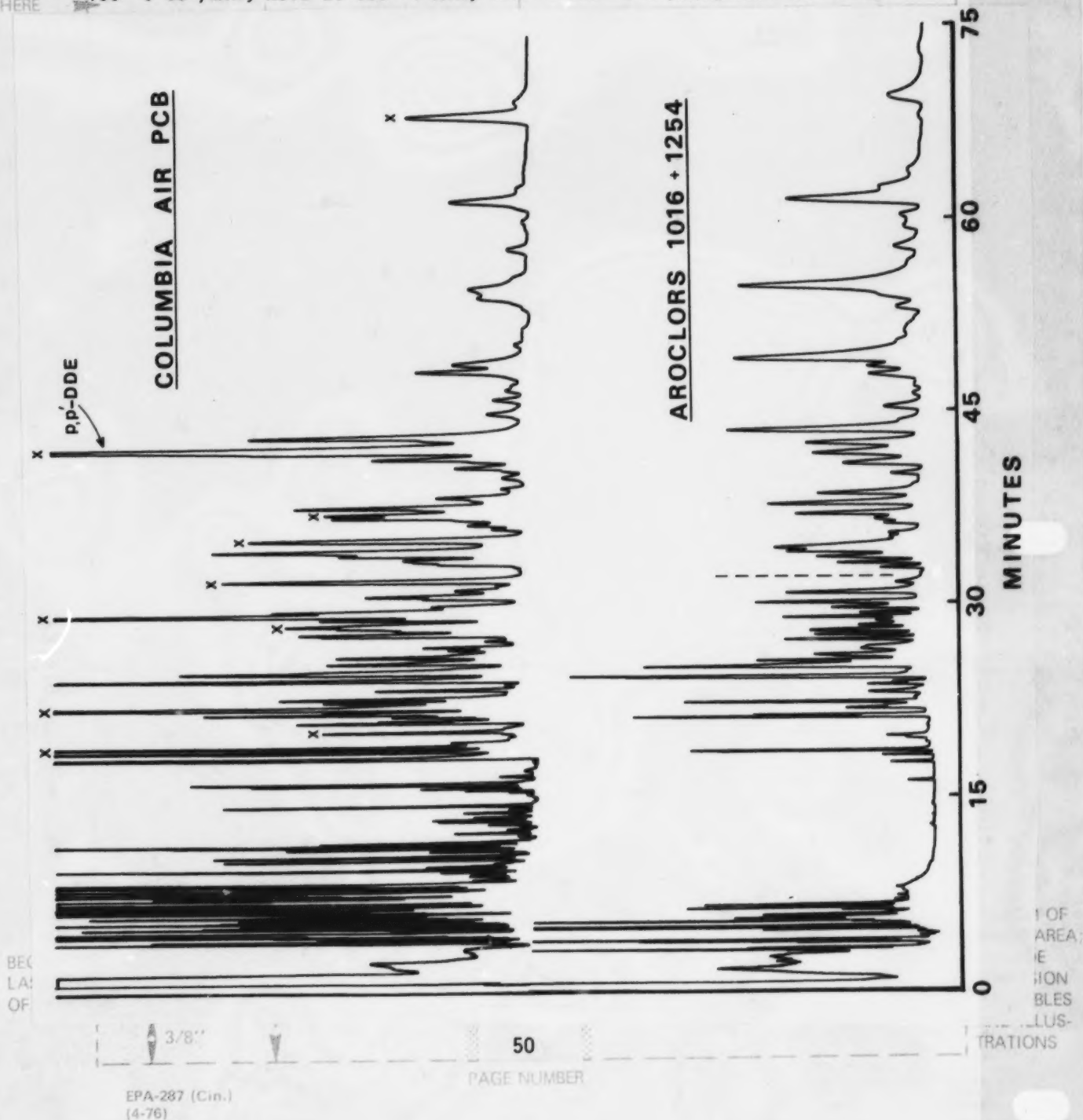
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Figure 14. Glass capillary chromatograms of the PCB fraction (silicic acid fraction 2, Table 4) of Columbia, S.C. air sample (July 14, 1979) collected on Tenax-GC resin treated with alcoholic KOH and 7% fuming H_2SO_4 , and a mixed Aroclor 1016-1254 standard (division indicated by dotted line). Major peaks which do not match the Aroclor patterns are indicated with an (X). 30 m SP-2100, Grob injection technique. Program: 45°C, hold 2 min, 45° - 150° @ 30°/min, hold at 150° 1 min, 150° - 200° @ 3°/min, hold at 200°.



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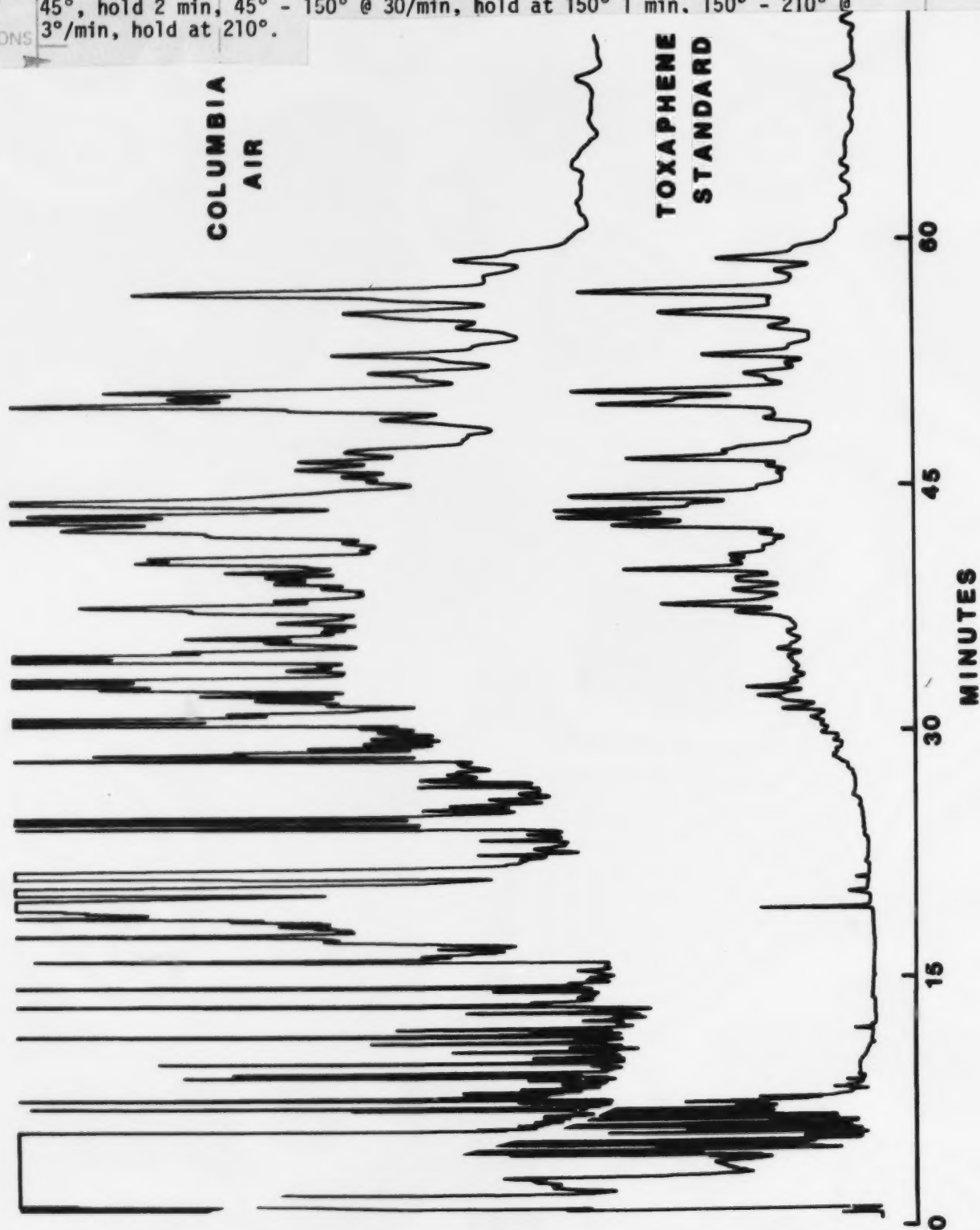
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Figure 15. Glass capillary chromatograms of the toxaphene fraction (silicic acid fraction 4, Table 4) of a Columbia, S.C. air sample (July 14, 1979) collected on Tenax-GC resin and a toxaphene standard (also fractionated on silicic acid). 30 m SP-2100, Grob injection technique. Program: 45°, hold 2 min, 45° - 150° @ 30/min, hold at 150° 1 min, 150° - 210° @ 3°/min, hold at 210°.



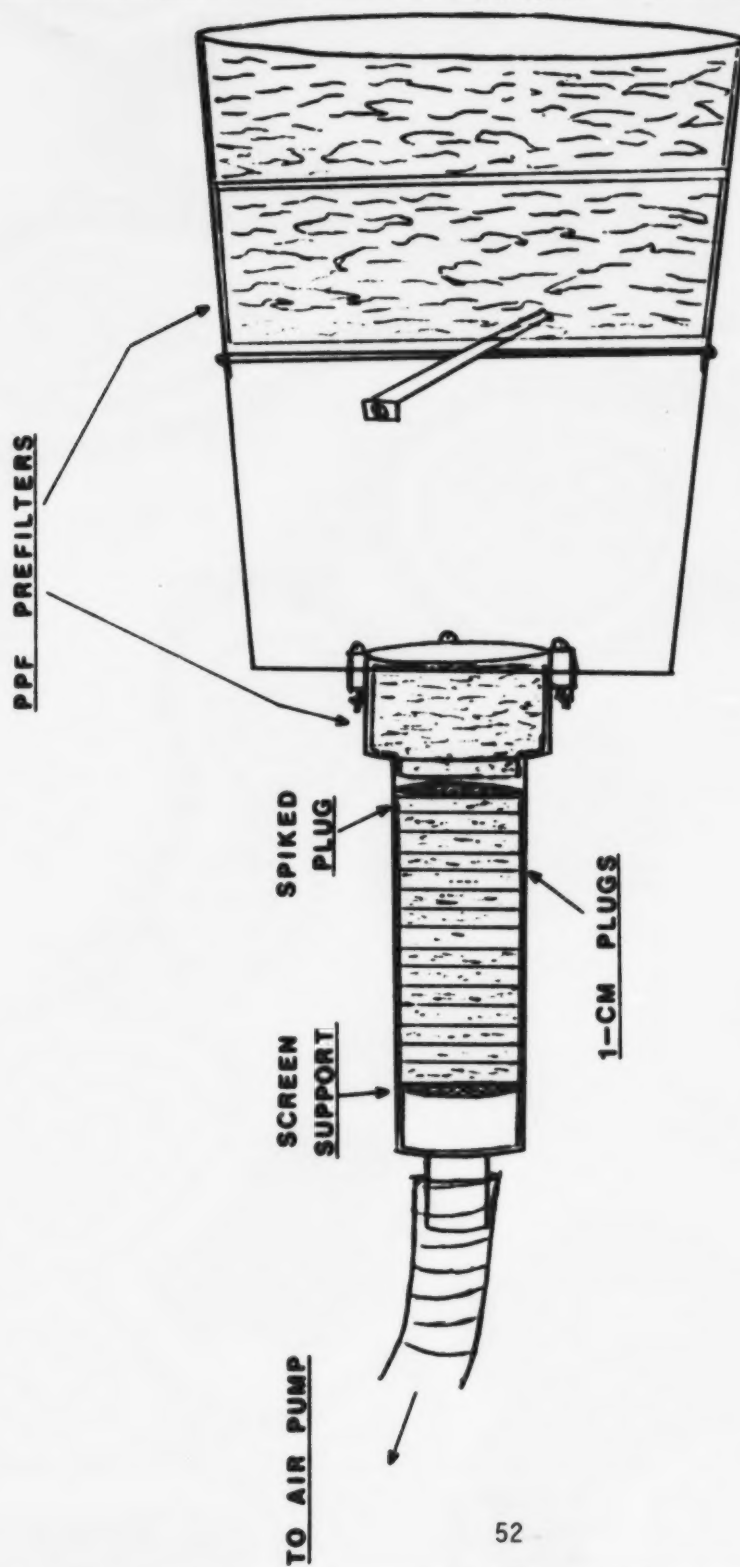


Figure 16. Apparatus for studying the elution of PCB isomers through PUF.

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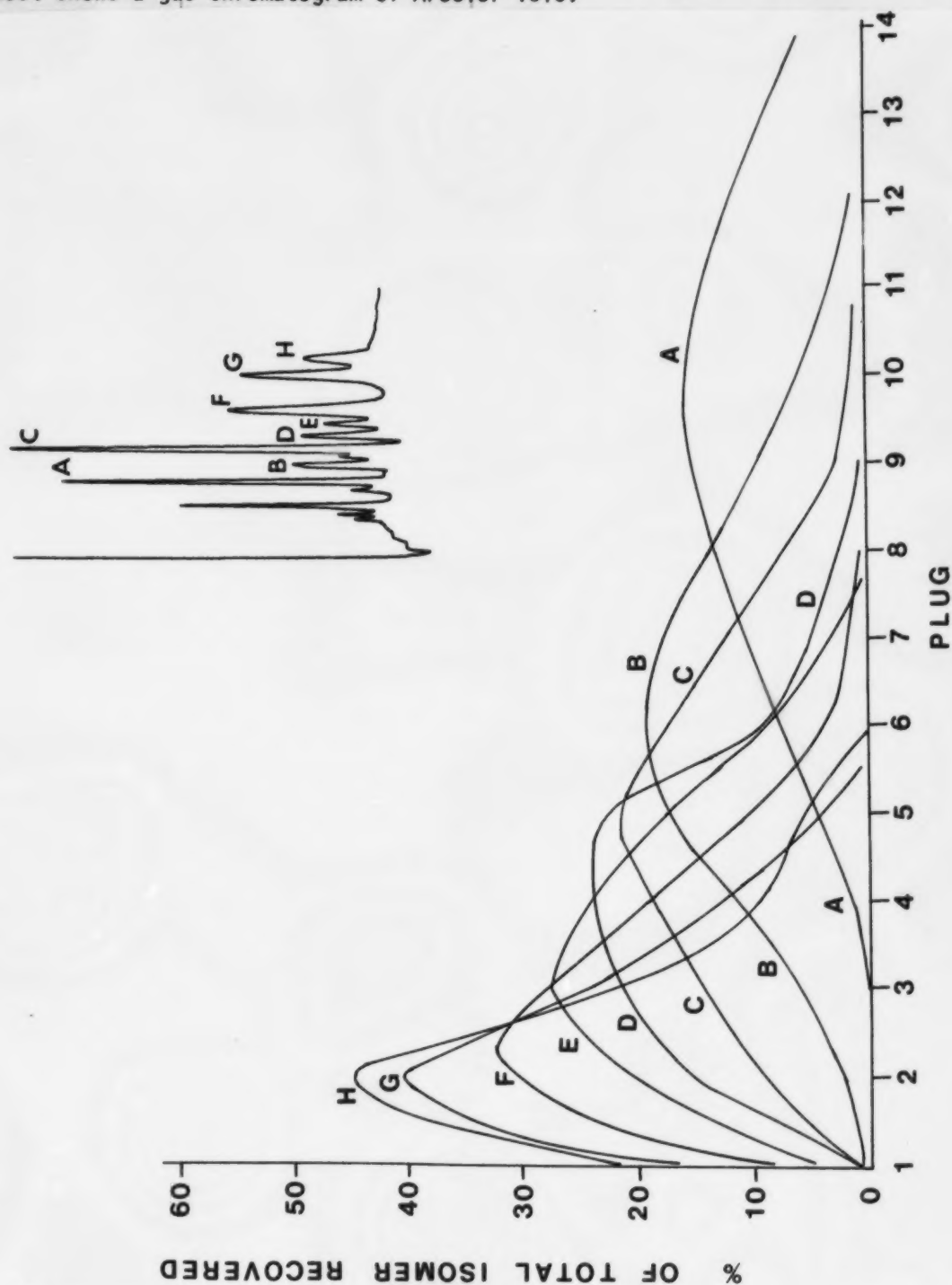
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Figure 17. Movement of Aroclor 1016 components through PUF, 760 m³ air, 0.5 m³/min. For clarification, the experimental points are not shown. Inset shows a gas chromatogram of Aroclor 1016.



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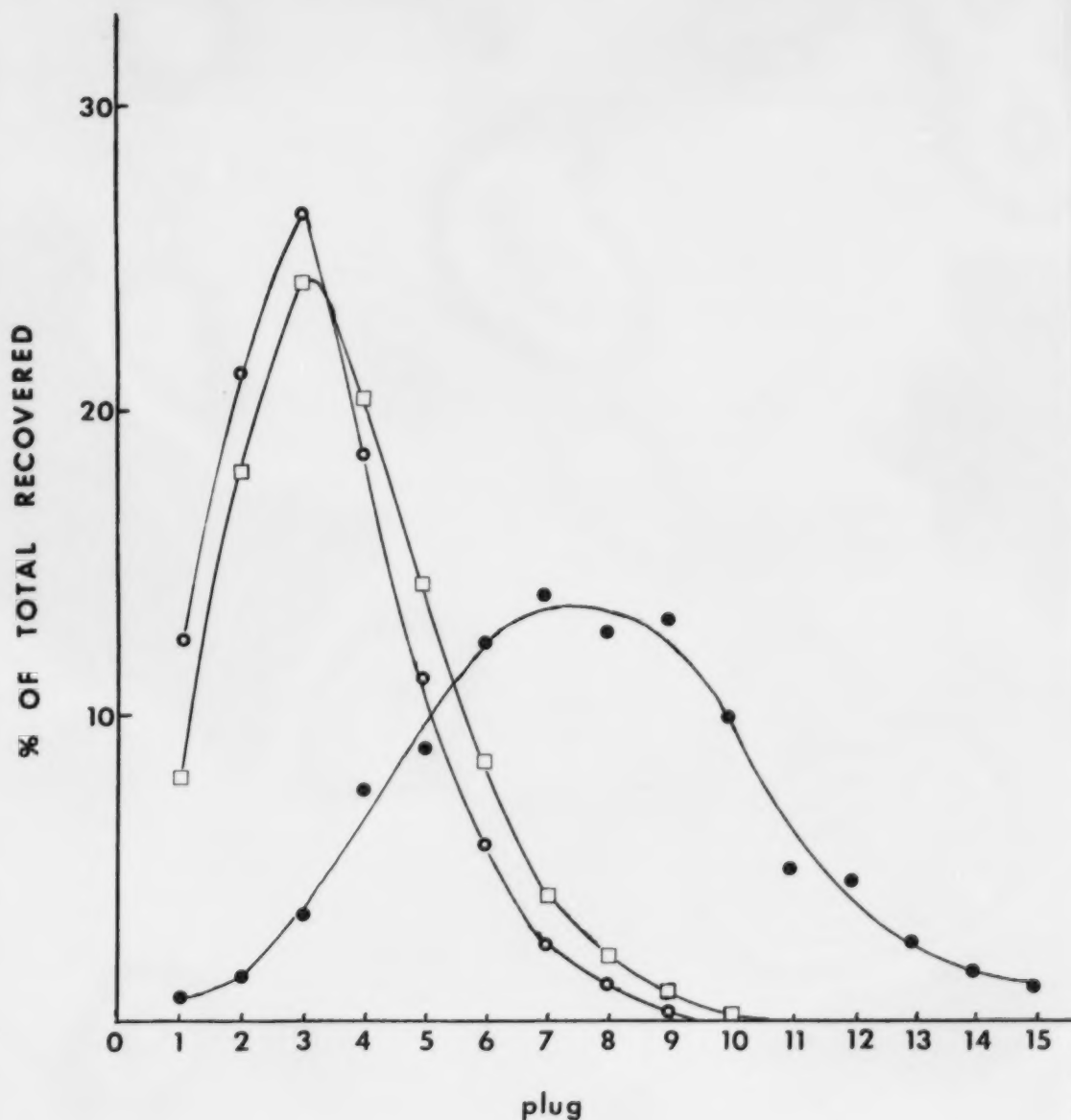
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Figure 18. Elution of light PCB isomers through PUF, 600 m³ air, 0.5 m³/min.
O = 2', 3,4-TCB. □ = 2,4'-5-TCB. ● = 3,3'-DCB.

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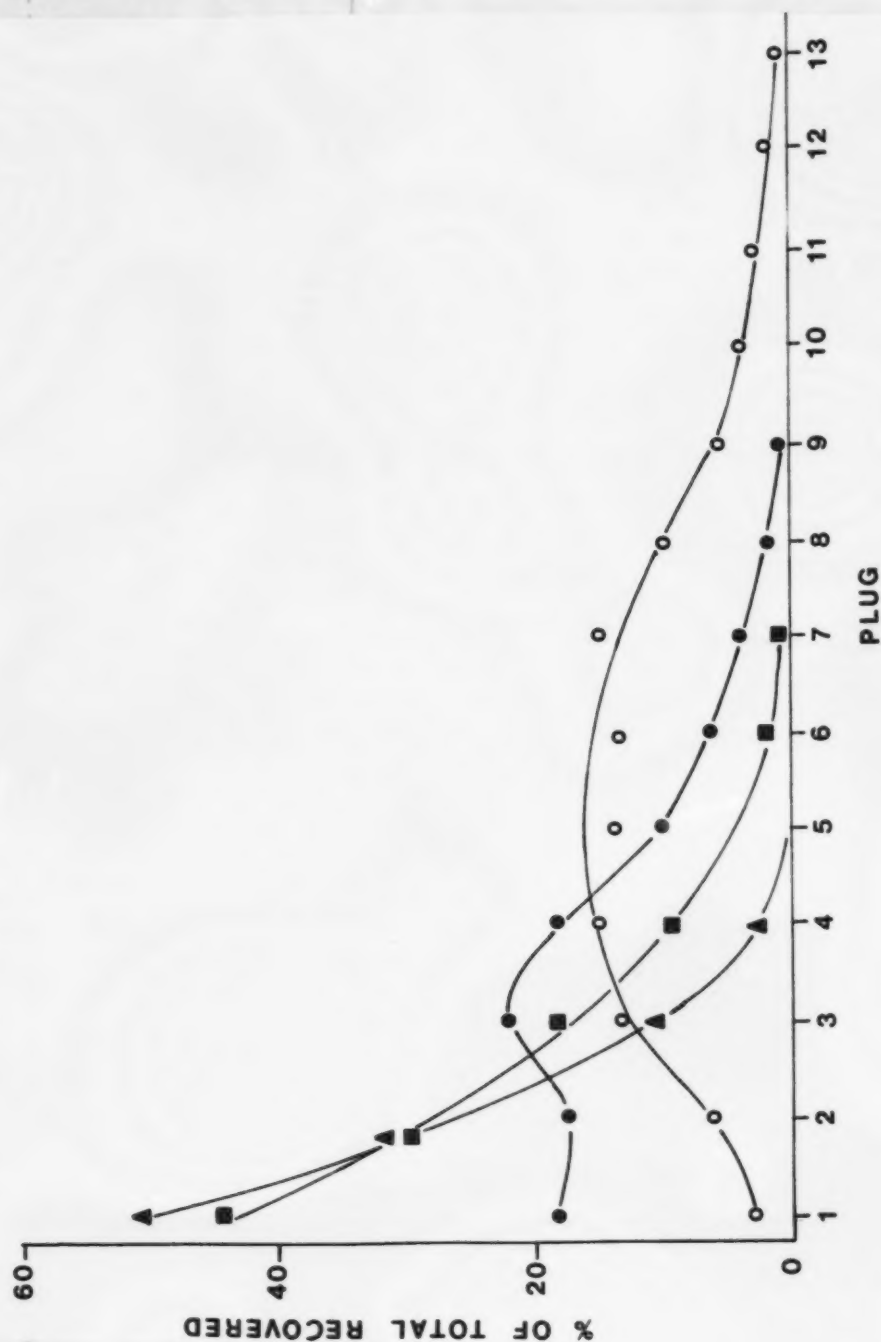
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Figure 19. Elution of heavy PCB isomers through PUF, 1620 m³ air, 0.5 m³/min.
○ = 2,2'-5,5'-TCB. ● = 3,3'-4,4'-TCB. ■ = 2,2',4,5,5'-PCB.
▲ = 2,2',4,4',6,6'-HCB.



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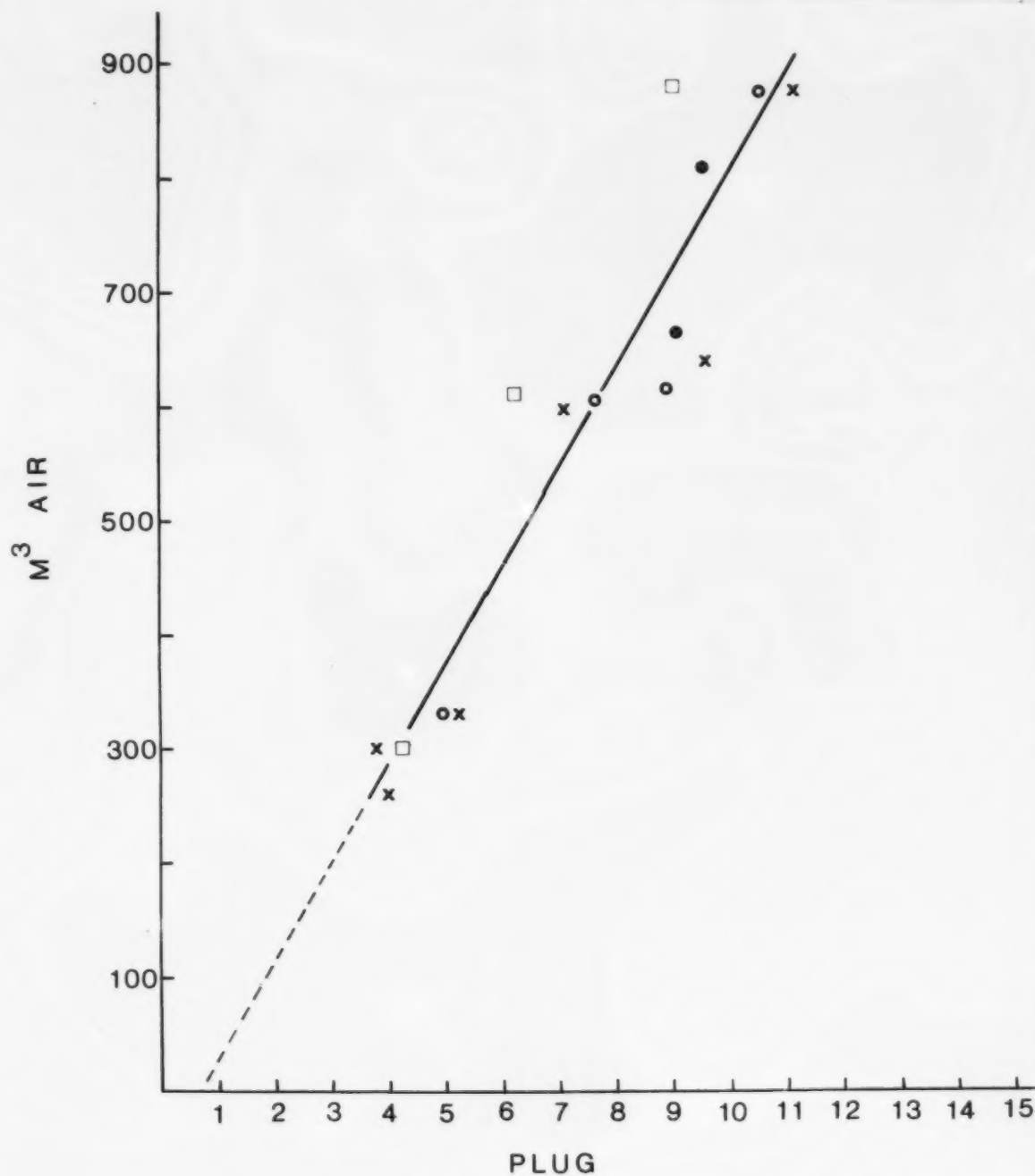
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Figure 20. Penetration of 3,3'-DCB peak maximum through PUF with total air volume. Flow rates (m^3/min): X = 0.15 - 0.22, O = 0.43 - 0.48, ● = 0.47 - 0.55, □ = 0.81.

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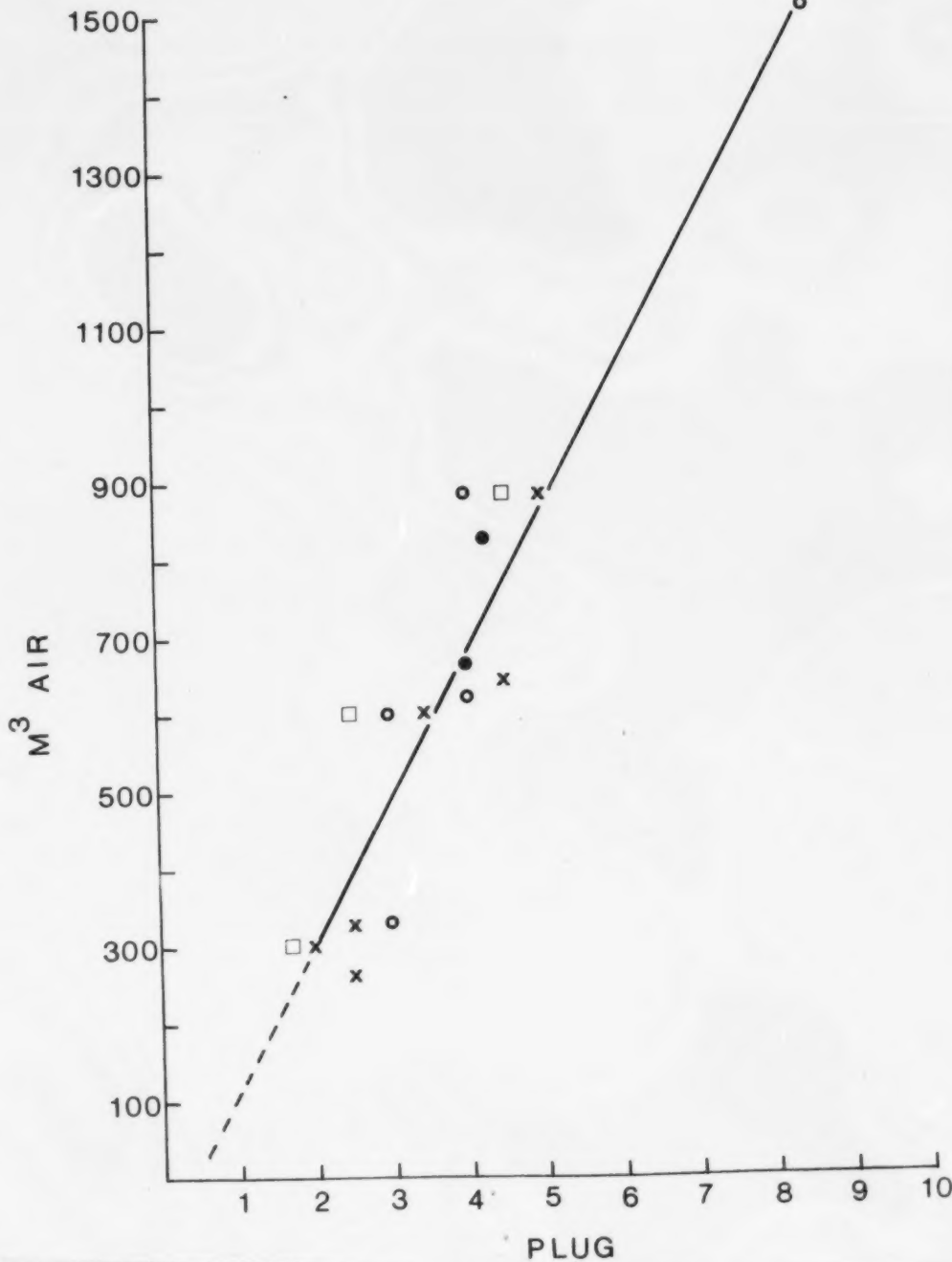
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Figure 21. Penetration of 2,4'-5-TCB peak maximum through PUF with total air volume. Symbols as in Figure 20.

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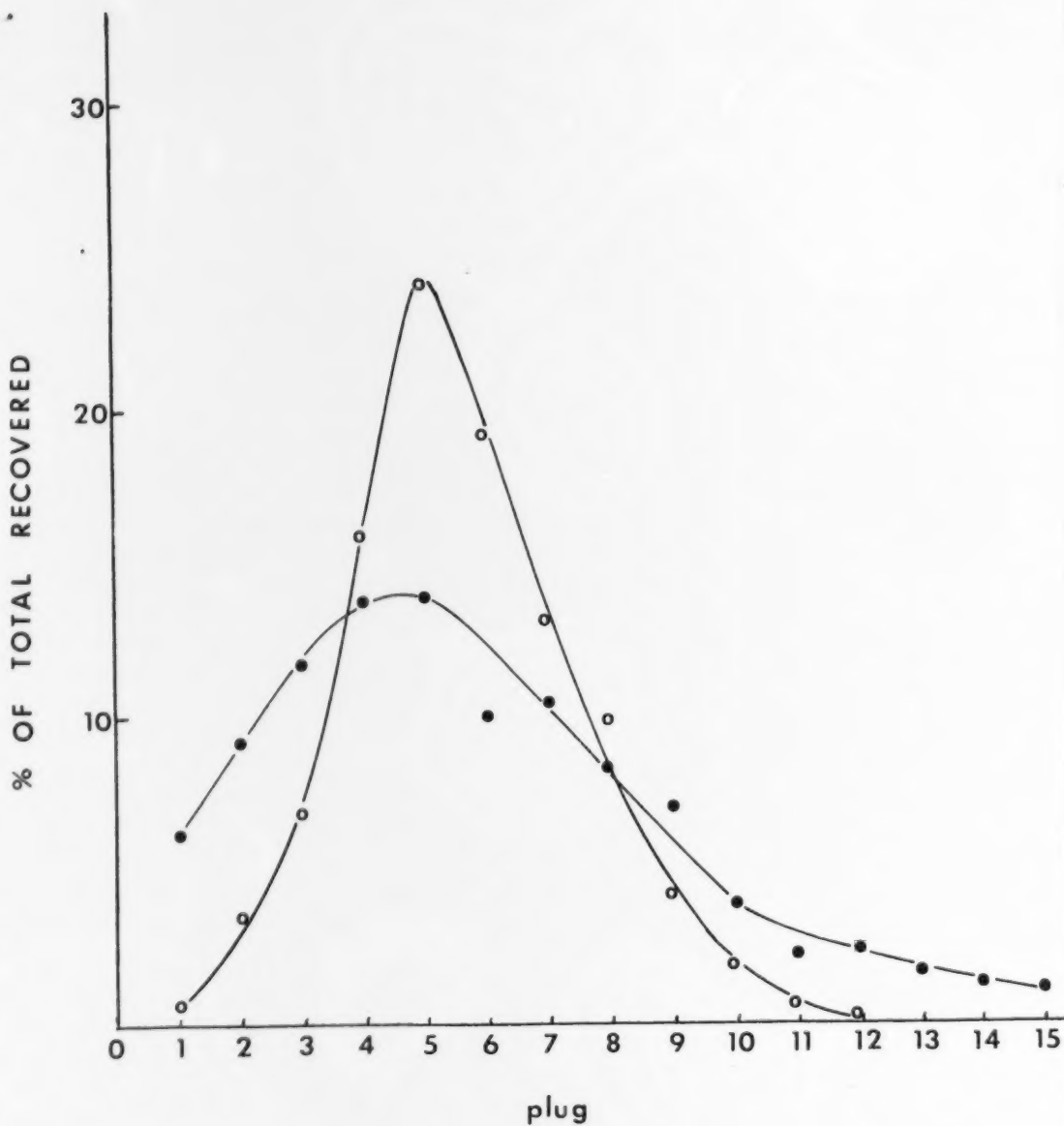
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Figure 22. Effect of flow rate on 2,4',5-TCB elution bands, 880 m³ air volume. Flows (m³/min): ○ = 0.22, ● = 0.81.

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